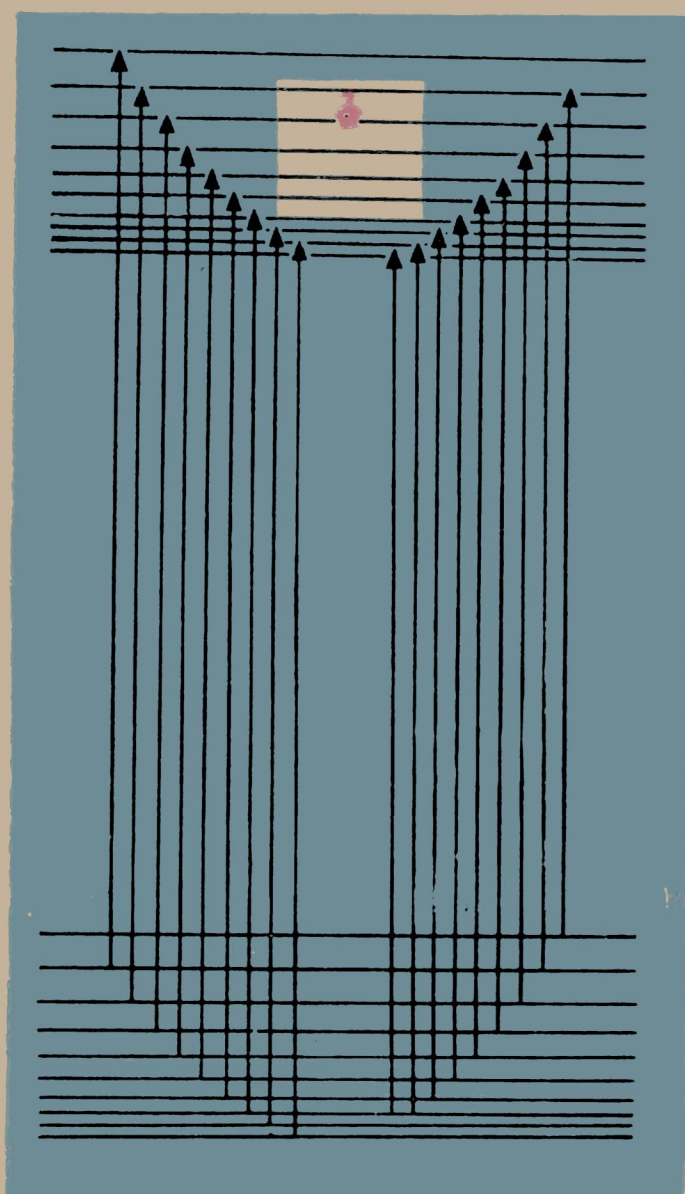


Problems
and Exercises in
**Physical
Chemistry**

E.V. Kiselyova, G. S. Karetnikov,
and I.V. Kudryashov



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Foreword

Chemical engineers and technologists (process engineers) must not only know the laws of physical chemistry, but also be able to use them judiciously in solving the problems in a particular field of their work. Solution of problems helps better assimilate the theory and contributes to its deeper understanding. The authors have tried to select problems covering virtually every aspect of the course in physical chemistry and pertaining to different chemical specialties.

To make sure that the student learns how to use reference books, the authors have excluded the values that can be found in readily available handbooks from most problems presented here. This book is divided into three parts: "Basic Theory of Physical-Chemistry Calculations", "Equilibrium State of Systems", and "Kinetics and Catalysis". Each chapter begins with the fundamental equations and symbols which are followed by problems with solutions, problems to be solved independently, and multivariant problems. Answers to the problems in the second category are provided at the end of the book. The multivariant problems have been written so as to allow the teacher to give an individual assignment to every student in the group. They are recommended for unassisted work. Multivariant problems may also be approached as single-variant ones with the teacher selecting out of the 15 to 25 choices available the one that suits best an individual student from the standpoint of his or her specialization.

In preparing the present edition, the authors took into account the main changes in the physical chemistry course and the recent trends that have established themselves in this field. They also acted in line with the general desire to reinforce the overall theoretical training of chemical and process engineers, which has recently been voiced by many a representative of the higher education establishment. This has prompted the authors to include a number of new chapters. The sequence in which the chapters are presented follows more closely the rigorous logic of the course: the geometrical parameters and energetic properties of molecules come first (Chapters 1 through 5), these are followed by analysis of the properties of substances in the ideal gaseous state, the next logical step being the real gaseous and condensed states of individual substances (Chapters 10 through 12).

Once the properties of individual substances have been covered, multiple-component systems in one or more phases are dealt with in Chapters 13 through 17. The more complex systems involved in chemical reactions are considered at equilibrium (Chapters 19 through 21) and in dynamics (from Chapter 23 on). The newly introduced chapters are representative of recent advances in physical chemistry.

In view of the general tendency to curtail supervised studies in the classroom in favour of independent work, emphases have been shifted accordingly. The theoretical introductions have been significantly cut down. In this respect, the authors' intent was to offer something different from a mere textbook. Primary emphasis has been placed on problems with solutions, which must serve as reference in cases where the student finds it difficult to use the right solution in his or her independent work.

This edition includes problems whose solution calls for the use of calculators. These problems are marked by asterisks. Presented at the end of some chapters are complex problems. Their solution requires knowledge of several topics from the course in physical chemistry. They may be recommended for term assignments.

The multivariant problems can be divided into two major categories: (1) problems covering the entire topic of the chapter to which they belong, whose solution requires the use of plots and handbooks and which are recommended for home assignments after the student has gone through the theoretical part and problems with solutions, and (2) problems dealing with a particular part of the chapter, which can be solved without involved calculations and plots and are recommended for testing. Multivariant problems typically include 25 assignments. In cases where no experimental data are available, an assignment may be presented under two or three variant numbers.

All values encountered throughout the book are in SI units with a few exceptions when they are given in other units still in common use.

This edition has been prepared with due account for the remarks and critical comments from the teachers of the Physical Chemistry Department of the D.I. Mendeleev Institute of Chemical Engineering in Moscow and other institutes.

International System of Units

The metric system of units of length, mass, force, and other physical quantities was developed during the French Revolution of 1789-94. Its simplicity and convenience have brought it into universal use. In scientific research, metric units have been substituted for the previously used units of measurement. The most extensive and

improved form of the metric system, known as the International System (or sometimes simply SI after the French name "système international"), was adopted officially by the General Conference on Weights and Measures in 1960.

The SI unit of mass is the kilogram (kg) defined as the mass of the international standard made of a platinum-iridium alloy and kept at the International Bureau of Weights and Measures in Paris. At present, there is one inconsistency in the SI system, which lies in the fact that the name of the unit of mass has the prefix "kilo". This inconsistency will persist until consensus is reached on the new name and symbol of the unit of mass. In the meantime, it should be remembered that one milligram, written as 1 mg, rather than one microkilogram, equals one millionth of the unit of mass, and not one thousandth as would be inferred from the prefix "milli".

The unit of length in the SI system is the metre (m). Previously, the metre was defined as the distance between two notches on the platinum-iridium standard also kept at the International Bureau of Weights and Measures in Paris. In 1960, an international agreement was reached to define the metre as the length equal to 1 650 763.73 wavelengths of the radiation corresponding to the orange-red line in the spectrum of krypton-86.

The SI unit of time is the second (s) which is defined as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between two hyperfine levels of the ground state of the cesium-133 atom at a wavelength approximately equal to 3.26 cm. In the past, the second was defined as 1/86 400 the mean solar day.

The unit of volume in the SI system is the cubic metre (m³). In chemistry, wide use is made of the litre (l) as the unit of volume, which equals 1/10³ m³. A millilitre, 1 × 10⁻³ litre, is equal to one cubic centimetre: 1 ml = 1 cm³.

The SI unit of force, the newton (N), is defined as the force imparting an acceleration of 1 m s⁻² to a mass of 1 kg in the direction of the force. A newton equals 10⁵ dynes (a dyne being the unit of force in the CGS system, equal to the force which imparts an acceleration of 1 cm s⁻² to a 1 g mass).

The unit of energy in the SI system is the joule (J) which is the work done by a force of magnitude of 1 N when the body to which it is applied is displaced 1 m in the direction of the force: 1 J = 1 N × 1 m = 10⁷ erg = 10⁷ dyne cm.

Formerly, the calorie was widely used as the unit of energy. The thermochemical calorie defined as 4.184 J is approximately equal to the amount of energy required to heat 1 g of water by 1 °C. The large calorie (kcal) equals 10³ cal. The following conversion factors are good to remember: 1 cal = 4.184 J; 1 kcal = 4.184 kJ.

Sym- bol	Name of quantity	SI unit	Units widely used before 1963	Factor of conversion into SI
<i>W</i>	Work done by the system	J/mole	litre atm/mole	1.0133×10^3
<i>a</i>	Activity	—	kcal/mole	4.187×10^3
<i>a</i>	Van der Waals constant	$(\text{m}^3)^2 \text{ kmole}^{-2} \text{ N/m}^2$	—	—
			litre ² atm/mole ²	1.0133×10^{-1}
<i>b</i>	Van der Waals constant	$\text{m}^4 \text{ N/kmole}^2$	—	—
<i>C</i>	Heat capacity	m^3/kmole	litre/mole	1
<i>D</i>	Permittivity	$\text{J mole}^{-1} \text{ deg}^{-1}$	cal mole ⁻¹ deg ⁻¹	4.187
<i>d</i>	Density	—	—	—
<i>E</i>	Energy	kg/m ³	g/cm ³	10^3
<i>F</i>	Electromotive force	J	erg	10^{-7}
Φ	Electrode potential	V	V	1
<i>A</i>	Helmholtz energy (isochoric-isother- mal potential)	V	V	1
		J/mole	kcal/mole	4.187×10^3
<i>F</i>	Force	N	dyne	10^{-5}
<i>G</i>	Gibbs' energy (isobaric isothermal po- tential)	J/mole	kcal/mole	4.187×10^3
<i>m</i>	Mass	kg	g	10^{-3}
<i>H</i>	Enthalpy	J/mole	kcal/mole	4.187×10^3
<i>I</i>	Rotational moment of inertia	kg m ²	g cm ²	10^{-7}
<i>I</i>	Ionization potential	J/mole	eV/mole	9.6505×10^4
<i>j</i>	Rotational quantum number	—	—	—
<i>K_a</i>	Chemical equilibrium constant	—	—	—
<i>K_{cr}</i>	Cryoscopic constant	deg 10 ³ kg/kmole	deg g mole	1

K_{eb}	Ebullioscopic constant	$\text{deg } 10^3 \text{ kg/kmole}$	$\text{deg } 10^3 \text{ g/mole}$	1
K	Distribution coefficient	—	—	—
k	Reaction rate constant	—	—	—
l	Length	m	cm	10^{-2}
m	Molality	kmole/1 000 kg	mole/1 000 g	1
c	Molarity	kmole/m^3	mole/litre	1
x	Molar fraction	—	—	1
N	Number of molecules	—	—	1
n	Number of moles	—	—	1
n	Refractive index	—	—	1
P	Parachor	$\text{kg}^{1/4} \text{ m}^3 \text{ s}^{-1/2} \text{ kmole}^{-1}$	$\text{g}^{1/4} \text{ cm}^3 \text{ s}^{-1/2} \text{ mole}^{-1}$	1.779×10^{-4}
P	Pressure	$\text{Pa (N/m}^2\text{)}$	mm Hg	1.333×10^2
P	Partial pressure	$\text{Pa (N/m}^2\text{)}$	atm	1.0133×10^5
			mm Hg	1.333×10^2
Q, q	Heat	J	cal	4.187
R	Molar refraction	m^3/kmole	cm^3/mole	10^{-3}
r	Refractivity	m^3/kg	cm^3/g	10^{-3}
ρ	Resistivity	ohm m	ohm cm	10^{-2}
r	Radius	m	Å	10^{-10}
S	Entropy	$\text{J deg}^{-1} \text{ kmole}^{-1}$	$\text{cal deg}^{-1} \text{ mole}^{-1}$	4.187×10^3
T	Temperature	deg K	°C	$t + 273.15$
t	Transfer number	—	—	1
U	Internal energy	J/kmole	kcal/mole	4.187×10^3
u	Velocity of gas molecules	m/s	cm/s	10^{-2}
v	Absolute velocity of ions	$\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	10^{-4}
V	Dilution	m^3/kmole	litre/mole	1
V	Volume	m^3	litre	10^{-3}
v	Vibrational quantum number	—	—	1
z	Number of collisions	—	—	—

(Table concluded)

Sym- bol	Name of quantity	SI unit	Units widely used before 1963	Factor of conversion into SI
L	Partial quantity	—	—	—
α	Degree of dissociation	—	—	1
α	Polarizability	m^3	cm^3	10^{-3}
γ	Activity coefficient	—	—	1
Δ	Final change in a property	—	—	—
e	Binding energy	J/kmole	kcal/mole	4.187×10^6
η	Viscosity	$Pa\ s\ (N\ s/m^2)$	cP	10^{-3}
χ	Electrical conductivity	$mho\ m^{-1}$	$mho\ cm^{-1}$	10^{-2}
λ	Equivalent conductivity	$mho\ m^2/kg\text{-}eq$	$mho\ cm^2/g\text{-}eq$	10^{-1}
λ	Wavelength	m	Å	10^{-10}
μ	Electric dipole moment	C m (m s A)	$10^{-18}\ e.s.u.$	0.333×10^{-11}
μ	Chemical potential	—	—	1
ν	Frequency	s^{-1}	s^{-1}	1
π	Osmotic pressure	Pa (N/m ²)	atm	1.0133×10^5
π	Reduced pressure	—	—	1
σ	Surface tension	N/m	dyne/cm	10^{-3}
σ	Gas-kinetic diameter	m	Å	10^{-10}
t	Time	s	s	1
τ	Reduced temperature	—	—	1
$\sim \nu$	Wave number	m^{-1}	cm^{-1}	10^2

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Values of Some Physical and Chemical Constants

Avogadro constant	$N_A = 6.0229 \times 10^{24} \text{ mole}^{-1}$
Velocity of light	$c = 2.997925 \times 10^8 \text{ m/s}$
Electron mass	$m = 9.1083 \times 10^{-31} \text{ kg}$
Electron charge	$e = 1.60206 \times 10^{-19} \text{ C}$
Faraday	$F = N_A e = 96\,490 \text{ C/mole}$
Dalton	$D = 1.66033 \times 10^{-27} \text{ kg}$
Planck constant	$h = 6.6252 \times 10^{-34} \text{ J s}$
Quantum of angular momentum	$\hbar = h/2\pi = 1.05443 \times 10^{-34} \text{ J s}$
Proton mass	$m_p = 1.67239 \times 10^{-27} \text{ kg}$
Neutron mass	$m_n = 1.67470 \times 10^{-27} \text{ kg}$
Boltzmann constant	$k = 1.3805 \times 10^{-23} \text{ J/deg}$
Gas constant per mole	$R = N_A k = 8.3146 \text{ J mole}^{-1} \text{ K}^{-1}$
Gas constant	$R = 0.08206 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$
Standard molar volume of gas at 273 K and $1.013 \times 10^5 \text{ Pa}$	22.415 litre
Centigrade temperature	$t^\circ\text{C} = T\text{K} - 273.15$
Atmospheric pressure	1 atm = 101.325 kN m ⁻²
Electric dipole moment	$0.1602 \times 10^{-28} \text{ C m (4.8029 D)}$
Electron-volt	1 eV = 96.4905 kJ/mole

CHAPTER 1

Fundamentals of Quantum Chemistry. The Chemical Bonding Theory and the LCAO-MO Method

Basic Equations and Symbols

According to the linear combination of atomic orbitals approximation (LCAO-MO method), the wave function is given by the equation

$$\psi = C_A \psi_A + C_B \psi_B \quad (1.1)$$

where ψ is the molecular wave function, C_A and C_B are coefficients, and ψ_A and ψ_B are atomic wave functions of atoms A and B. The potential energy of a system comprising atoms A and B is given by the equation

$$E_{\text{pot}} = \frac{Z_A Z_B}{r_{AB}} - \frac{Z_A e}{r_A} - \frac{Z_B e}{r_B} \quad (1.2)$$

where Z is the charge of the atomic nucleus, e is the electronic charge, r_{AB} is the internuclear distance, and r_A and r_B are the distances between the nucleus and an electron.

Schrödinger's equation is

$$\hat{H}\psi = E\psi \quad (1.3)$$

in which $\hat{H} = -\frac{h^2}{8\pi^2 m} \nabla^2 + E_{\text{pot}}$ is the Hamiltonian operator, E_{pot} is the potential energy, and ∇^2 is Laplace's operator.

For the diatomic molecule A—B,

$$\begin{aligned} (H_{AA} - ES_{AA}) C_A + (H_{AB} - ES_{AB}) C_B &= 0 \\ (H_{AB} - ES_{AB}) C_A + (H_{BB} - ES_{BB}) C_B &= 0 \end{aligned}$$

where $H_{AB} = H_{BA} = \int_{-\infty}^{+\infty} \psi_A \hat{H} \psi_B dv = \int_{-\infty}^{+\infty} \psi_B \hat{H} \psi_A dv$ is an exchange integral, $H_{AA} = H_{BB} = \int_{-\infty}^{+\infty} \psi_A \hat{H} \psi_A dv = \int_{-\infty}^{+\infty} \psi_B \hat{H} \psi_B dv$ is a coulombic integral, $S_{AB} = S_{BA} = \int_{-\infty}^{+\infty} \psi_A \psi_B dv$ is an overlap integral, and v is the volume.

For polyatomic molecules, the LCAO-MO method provides a system of n equations, n being the number of atoms in a molecule:

$$\sum (H_{ij} - ES_{ij}) C_j = 0 \quad (1.4)$$

where i is the equation number, and j is the number of the term in the equation.

We shall have non-zero roots of the system of equations (1.4) if the determinant is zero:

$$|H_{ij} - ES_{ij}| = 0 \quad (1.5)$$

Application of the LCAO method to homonuclear diatomic molecules of the second period in Mendeleev's periodic system gives the

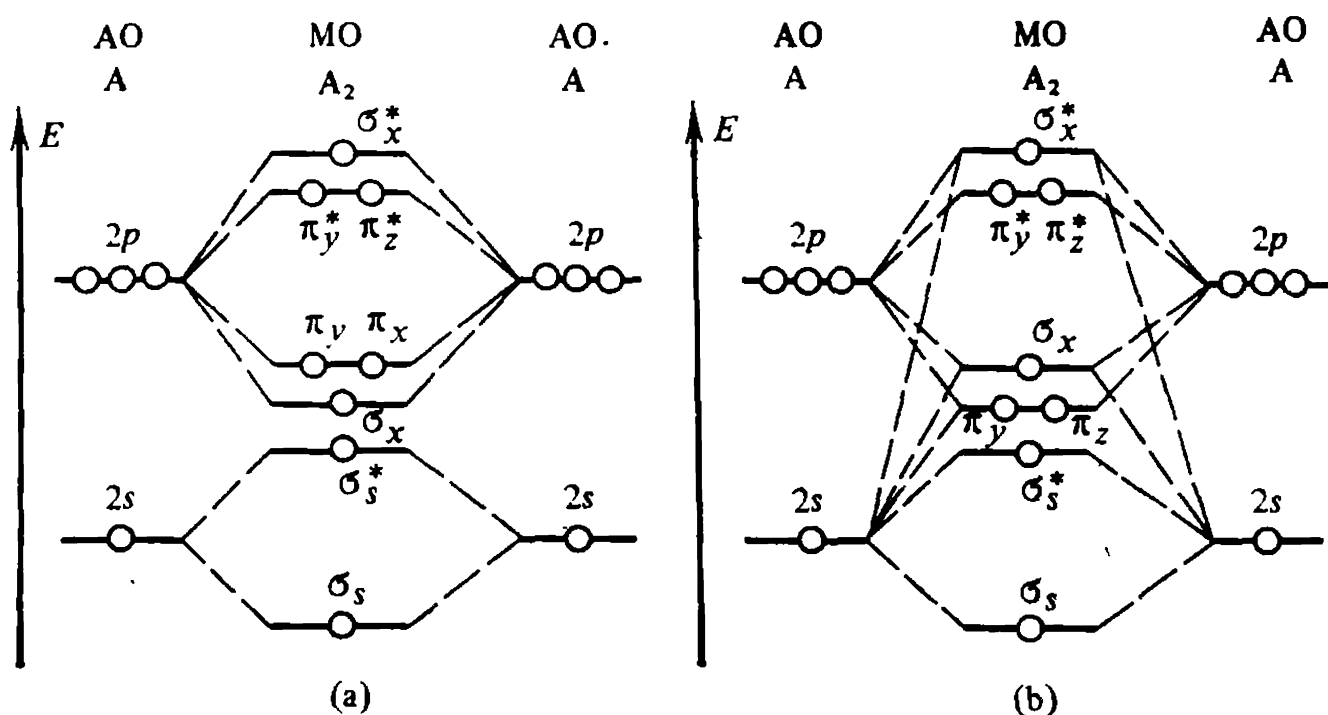


Fig. 1. Relative arrangement of molecular orbitals according to energies of homonuclear diatomic molecules: (a) without σ_s - and $\pi_y \pi_z$ -MO interaction and (b) with such interaction

atomic orbitals (AO) $2s$, $2p_x$, $2p_y$, and $2p_z$. Let us assume that the x axis coincides with the molecular axis. In the $A-A$ atomic system its orientation is towards the two atoms. The atomic orbital of the $2s$ electron has a spherical symmetry, the overlap of the $2s$ and $2p_x$ atomic orbitals being symmetrical about the molecular axis. Such molecular orbitals are known as σ -molecular orbitals. The overlap of the $2p_y$ and $2p_z$ atomic orbitals gives a π -molecular orbital. Such molecular orbitals are not symmetrical about the molecular axis. Rotation of a π -MO about the molecular axis through 180° results in reversal of the MO sign. Distinction is made between bonding σ -MO and antibonding σ^* -MO as well as between bonding π -MO and antibonding π^* -MO. The bond order is

$$u = \frac{1}{2} (n_b - n_a) \quad (1.6)$$

where n_b is the number of electrons on the bonding MO, and n_a is the number of electrons on the antibonding MO.

The sequence of MO energies is $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^*$. MO σ_{2p_x} , π_{2p_y} , and π_{2p_z} are close in terms of energy, and their places in the sequence of increasing energies are interchangeable. Figure 1 represents an energy-level diagram without (a) and with (b) interaction between 2s and 2p AO for homonuclear diatomic molecules. The AO and MO energies for heteronuclear diatomic molecules of the AB type, if the atom B is more electronegative, are shown in Fig. 2. The contribution of the atom B to the bonding MO is greater than that of the atom A, and, correspondingly, its contribution to the antibonding MO is less significant.

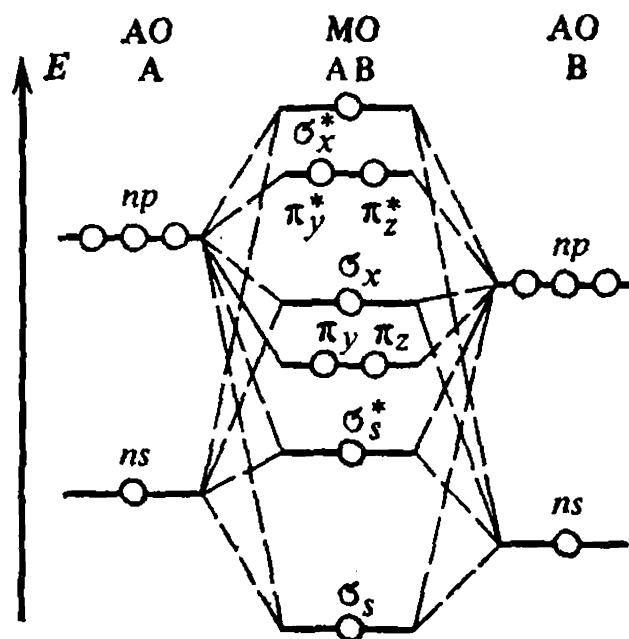


Fig. 2. Relative arrangement of molecular orbitals according to energies of heteronuclear diatomic molecules

The electronic states of the molecules are classified according to angular momentum and spin. Particular values of the quantum number m_l (Table 1) correspond to different types of MO.

TABLE 1. Quantum Numbers Corresponding to Particular MO

Atomic orbitals	Molecular orbitals	m_l
s, p_x, d_{x^2}	σ	0
p_y, d_{xy}, d_{xz}	π	± 1
$d_{yz}, d_{y^2-z^2}$	δ	± 2

The electronic state term is written as

$$^{2S+1} |M_L| \quad (1.7)$$

where S is the total spin of the electrons in a molecule, and M_L is the total angular momentum of the electrons. The symbols of the total angular momentum are given below.

State symbol	Σ	π	Δ
M_L	0	± 1	± 2

Exercises

1. Determine the MO energy of the ion H_2^+ using the LCAO-MO method.

Solution. Write the MO energy from Eq. (1.3):

$$E = \frac{\psi \hat{H} \psi}{\psi^2} = \frac{\int_{-\infty}^{+\infty} \psi \hat{H} \psi \, dv}{\int_{-\infty}^{+\infty} \psi^2 \, dv}$$

Substitute ψ from Eq. (1.1) into this equation:

$$E = \frac{\int_{-\infty}^{+\infty} (C_A \psi_A + C_B \psi_B) \hat{H} (C_A \psi_A + C_B \psi_B) \, dv}{\int_{-\infty}^{+\infty} (C_A \psi_A + C_B \psi_B)^2 \, dv}$$

After the necessary transformation under the integrals in the numerator and denominator and substitution for exchange, coulombic, and overlap integrals we have

$$E = \frac{C_A^2 H_{AA} + 2C_A C_B H_{AB} + C_B^2 H_{BB}}{C_A^2 S_{AA} + 2C_A C_B S_{AB} + C_B^2 S_{BB}}$$

Since the energy during chemical bonding must be minimal, take the derivative $\partial E / \partial C_A$, according to the variational method, and equalize it to zero. Similarly, take the derivative $\partial E / \partial C_B$ and also equalize it to zero:

$$\frac{\partial E}{\partial C_A} = 2C_A H_{AA} + 2C_B H_{AB} - E (2C_A S_{AA} + 2C_B S_{AB}) = 0$$

$$\frac{\partial E}{\partial C_B} = 2C_A H_{AB} + 2C_B H_{BB} - E (2C_A S_{AB} + 2C_B S_{BB}) = 0$$

or derive two equations:

$$(H_{AA} - ES_{AA}) C_A + (H_{AB} - ES_{AB}) C_B = 0$$

$$(H_{AB} - ES_{AB}) C_A + (H_{BB} - ES_{BB}) C_B = 0$$

To determine the coefficients C_A and C_B in Eq. (1.1) solve the system of equations. We shall have solutions whose roots are non-zero if the determinant is zero:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$$

The solution of this determinant will be

$$(H_{AA} - E)^2 - (H_{AB} - ES)^2 = 0$$

$$E^2 - 2H_{AA} E + H_{AA}^2 - H_{AB}^2 + 2H_{AB} SE - E^2 S^2 = 0$$

Write the resulting equation as follows:

$$E^2 (1 - S^2) - 2 (H_{AA} - H_{AB}S) E + H_{AA}^2 - H_{AB}^2 = 0$$

The quadratic equation has two roots:

$$\begin{aligned} E_{1,2} &= \frac{(H_{AA} - H_{AB}S) \pm \sqrt{(H_{AA} - H_{AB}S)^2 - (1 - S^2)(H_{AA}^2 - H_{AB}^2)}}{1 - S^2} \\ &= \frac{(H_{AA} - H_{AB}S) \pm (H_{AB} - H_{AA}S)}{1 - S^2} \\ E_1 &= \frac{H_{AA}(1 - S) + H_{AB}(1 - S)}{1 - S^2} = \frac{H_{AA} + H_{AB}}{1 + S} \\ E_2 &= \frac{H_{AA}(1 + S) - H_{AB}(1 + S)}{1 - S^2} = \frac{H_{AA} - H_{AB}}{1 - S} \end{aligned}$$

Two different MO energies are thus obtained.

2. Determine the coefficients C_A and C_B in Eq. (1.1) for the ion H_2^+ .

Solution. In view of the fact that $S_{AA} = S_{BB} = 1$, because of the wave function being normalized, Eq. (1.4) yields

$$(H_{AA} - ES_{AA}) C_A + (H_{AB} - ES_{AB}) C_B = 0 \quad (a)$$

$$(H_{AB} - ES_{AB}) C_A + (H_{BB} - ES_{BB}) C_B = 0 \quad (b)$$

Substitute the value of E_1 , found in Problem 1, into Eq. (a):

$$\left(H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S} \right) C_A + \left(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} \right) C_B = 0$$

The difference in the first brackets is

$$\left(H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S} \right) = - \frac{H_{AB} - H_{AA}S}{1 + S}$$

The difference in the second brackets is

$$\left(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} S \right) = \frac{H_{AB} - H_{AA}S}{1 + S}$$

Consequently, the coefficients of C_A and C_B are equal but opposite in sign. Hence, $C_A = +C_B$. Substitute E_1 into Eq. (b):

$$\left(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} S \right) C_A + \left(H_{BB} - \frac{H_{AA} + H_{AB}}{1 + S} \right) C_B = 0$$

The difference in the first brackets is

$$\left(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} S \right) = \frac{H_{AB} - H_{AA}S}{1 + S}$$

The difference in the second brackets is

$$\left(H_{BB} - \frac{H_{AA} + H_{AB}}{1 + S} \right) = - \frac{H_{AB} - H_{BB}S}{1 + S}$$

hence $C_A = +C_B$. Substitute the energy E_2 from Problem 1 into Eq. (a). The difference in the first brackets is

$$\left(H_{AA} - \frac{H_{AA} - H_{AB}}{1 - S} \right) = \frac{H_{AB} - H_{AA}S}{1 - S}$$

The difference in the second brackets is

$$\left(H_{AB} - \frac{H_{AA} - H_{AB}}{1 - S} S \right) = \frac{H_{AB} - H_{AA}S}{1 - S}$$

The bracketed values are equal, hence $C_A = -C_B$. Substitute the energy E_2 into Eq. (b). The difference in the first brackets is

$$\left(H_{AB} - \frac{H_{AA} - H_{AB}}{1 - S} S \right) = \frac{H_{AB} - H_{AA}S}{1 - S}$$

The difference in the second brackets is

$$\left(H_{BB} - \frac{H_{AA} - H_{AB}}{1 - S} \right) = \frac{H_{AB} - H_{BB}S}{1 - S}$$

Hence, $C_A = -C_B$. Thus, the following two wave functions are derived:

$$\psi_1 = C_A \psi_A - C_A \psi_B$$

and

$$\psi_2 = C_A \psi_A + C_A \psi_B$$

The wave function must be normalized, that is $\int_{-\infty}^{+\infty} |\psi|^2 dv = 1$ because the ion H_2^+ must have only one electron within the entire available space. Substitute the derived wave function equations under the integral:

$$\begin{aligned} \int_{-\infty}^{+\infty} |\psi|^2 dv &= \int_{-\infty}^{+\infty} (C_A \psi_A - C_A \psi_B)^2 dv = \int_{-\infty}^{+\infty} C_A^2 \psi_A^2 dv \\ &\quad - 2 \int_{-\infty}^{+\infty} \psi_A \psi_B C_A^2 dv + \int_{-\infty}^{+\infty} C_A^2 \psi_B^2 dv = 1 \end{aligned}$$

But the coefficient C_A^2 is not equal to zero:

$$\int_{-\infty}^{+\infty} \psi_A^2 dv = \int_{-\infty}^{+\infty} \psi_B^2 dv = 1; \quad 2 \int_{-\infty}^{+\infty} \psi_A \psi_B dv = 0$$

Consequently,

$$\int_{-\infty}^{+\infty} \psi^2 dv = 1 - 0 + 1 = 2$$

The result is that the molecular wave function is not normalized. To make it normalized, it should be divided by $\sqrt{2}$. As a result, the following two normalized molecular wave functions are derived:

$$\psi_1 = \frac{1}{\sqrt{2}} \psi_A - \frac{1}{\sqrt{2}} \psi_B$$

and

$$\psi_2 = \frac{1}{\sqrt{2}} \psi_A + \frac{1}{\sqrt{2}} \psi_B$$

and the coefficients C_A and C_B will take the following values:

$$C_A = -C_B = 1/\sqrt{2} \quad \text{and} \quad C_A = C_B = 1/\sqrt{2}$$

3. Plot the functions ψ_1 , ψ_2 , ψ_1^2 , and ψ_2^2 , assuming that $\psi_1 = e^{-r_A} - e^{-r_B}$ and $\psi_2 = e^{-r_A} + e^{-r_B}$, where r_A and r_B are the distances from the nucleus of A or B to the electron. Establish, from the relationships of ψ_1^2 and ψ_2^2 with r , which of the two molecular functions, ψ_1 and ψ_2 , is more stable or, in other words, which of the molecular orbitals has less energy.

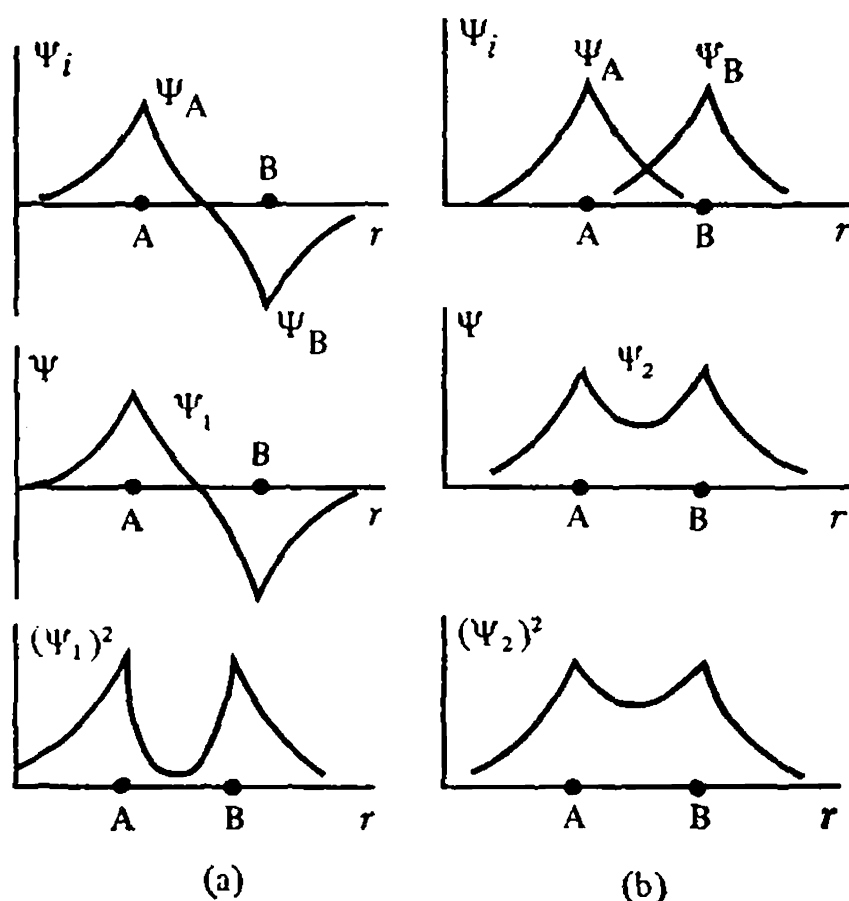


Fig. 3. Antibonding (a) and bonding (b) wave functions of a homonuclear diatomic molecule

Solution. The signs of ψ_A and ψ_B in the molecular wave function ψ_1 are opposite. These two functions are on the opposite sides of the abscissa (Fig. 3a). ψ_1^2 and ψ_2^2 are the probabilities of finding the electron at a given point in space. In the case of ψ_1^2 , the probability of

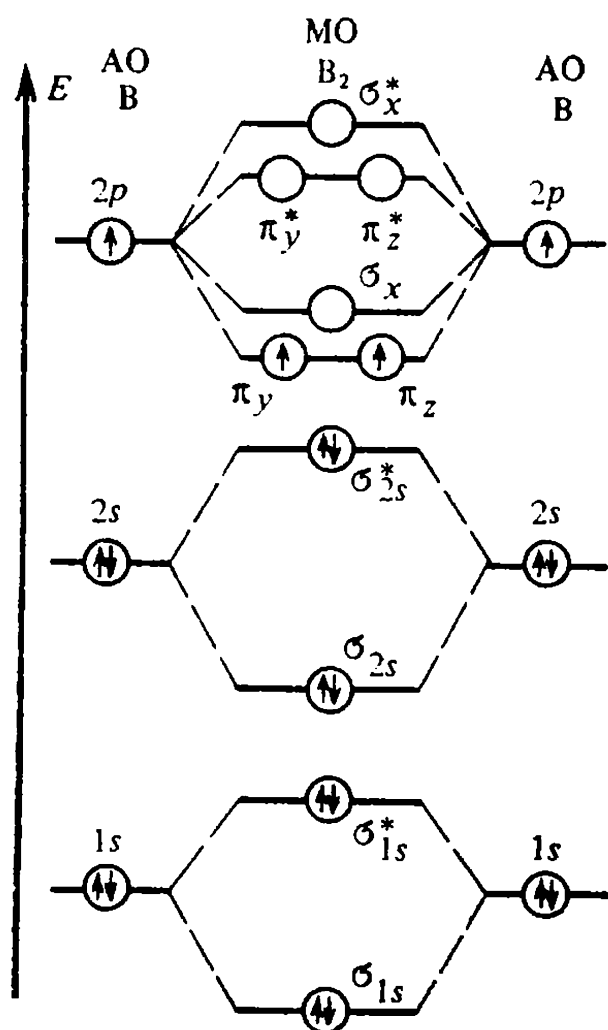


Fig. 4. Relative arrangement of electronic levels in molecule B_2 and filling of AO and MO with electrons

finding the electron in the space between the nuclei of A and B is nil. Therefore, the positively charged atomic nuclei repulse each other. Such a molecular orbital is called antibonding. As regards the wave function ψ_2 , the signs of ψ_A and ψ_B are similar. These functions lie on the same side of the abscissa (Fig. 3b). ψ_2^2 , which is the probability of finding the electron in the space between the nuclei of A and B, is not equal to zero. Hence, the positively charged atomic nuclei are attracted to the negatively charged space between the nuclei. Such a molecular orbital is known as bonding. Energy is required for the electron to be transferred from the bonding orbital to the antibonding one. Consequently, the energy of the bonding molecular orbital is lower than that of the antibonding orbital.

4. Plot the energy levels of the molecular orbitals of the

boron molecule B_2 . Determine the bond order. Boron molecules exhibit magnetic properties.

Solution. The atomic orbitals of each boron atom are $1s^2$, $2s^2$, and $2p^1$. The magnetic properties of the molecule B_2 indicate that the molecule has unpaired electrons. Apply Hund's law to the filling of the molecular orbitals with electrons. Then, the electronic configuration of the molecule B_2 may be written as

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_y) (\pi_z)$$

The $2s$ electrons affect the energy distribution among the π_x , π_y , and π_z electrons. Only this particular arrangement of electrons on the energy levels can account for the magnetic properties of the molecule B_2 . The relative positions of the energy levels are shown in Fig. 1, while Fig. 4 illustrates the relative positions of the electron

levels in the molecule B_2 and the way in which they are filled with electrons. Determine the bond order from Eq. (1.6):

$$u = \frac{1}{2} (6 - 4) = 1$$

Problems

1. Write the molecular orbitals of the molecule O_2 and the ions O_2^+ and O_2^- . Calculate the bond order in each particle. Arrange the bond energies in increasing order.

2. Draw the energy-level diagram for the molecule Li_2 . Arrange electrons on the energy levels. Determine the bond order. Find out whether the molecule Li_2 possesses magnetic properties.

3. Explain why the equilibrium internuclear distance in the molecule H_2 is 0.741×10^{-8} cm, whereas in the molecule Li_2 it is 2.672×10^{-8} cm.

4. Draw the energy-level diagram for the molecule O_2 . Determine the bond order. The molecule O_2 exhibits magnetic properties.

5. Write the MO of the molecule Be_2 . Determine the bond order. Find the internuclear distance and bond energy.

6*. Draw the energy-level diagram of the molecule BN. Determine the bond order. The molecule BN exhibits magnetic properties. The atom N is more electronegative than B.

7. Write the MO of the ion CO^+ and the molecules BO and CN. Determine the bond order in each particle. Define the term of the ground electronic state of all particles.

8. Proceeding from the electronic structures of the molecules BN, BO, and CO, arrange them in the order of the increasing bond energy.

Multivariant Problem

Write the MO of a compound and define the term of the ground elec-

Variant	Compound	Variant	Compound	Variant	Compound
1	BH	10	HBr	18	IBr
2	BF	11	HBr ⁺	19	ICl
3	BCl	12	CO	20	IF
4	BBr	13	ClF	21	NH
5	BeH	14	HCl	22	NO
6	BeF	15	HCl ⁺	23	NO ⁺
7	BeCl	16	HF	24	OH
8	BrCl	17	HI	25	OH ⁺
9	BrF				

tronic state. Determine the bond order. Establish whether the compound possesses magnetic properties.

CHAPTER 2

Geometrical Configuration of Atoms in Molecules. Elements of the Molecular Symmetry Theory

Basic Concepts and Symbols

The geometrical configuration of atoms in a molecule depends on the spatial orientation of the chemical bonds linking every atom. As regards the orientation of the chemical bonds, it is determined by the type of AO and MO. Figure 5 illustrates the expected equilibrium configurations of molecules depending on the number of the

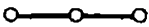
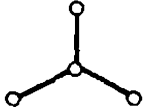

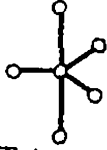



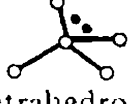
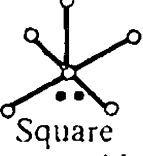

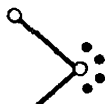


Number of unshared electron pairs	Number of binding electron pairs				
	2	3	4	5	6
0	 Linear $D_{\infty h}$	 Plane triangle D_{3h}	 Tetrahedron T_d	 Trigonal bipyramid C_{3v}	 Octahedron O_h
1	 Nonlinear C_{2v}	 Trigonal pyramid C_{3v}	 Distorted tetrahedron C_{2v}, C_{3v}	 Square pyramid C_{4v}	 Irregular octahedron
2	 Nonlinear C_{2v}	 T-shaped C_{2v}	 Plane square D_{4h}		

Fig. 5. Anticipated equilibrium geometrical configurations of molecules, depending on the number of binding and unshared electron pairs

binding electron pairs and that of unshared electron pairs. To determine the equilibrium configuration of a molecule, one must establish the number of σ - and π -bonds as well as the number of free electron pairs that are not involved in chemical bonding. Figure 5 can be used to determine the equilibrium configuration of atoms in a molecule.

Molecular symmetry is understood as the symmetry of arrangement of the nuclei of a molecule's atoms in the state of equilibrium. A molecule is said to be symmetrical if there occurs a linear ortho-

gonal transformation of coordinates, which leads to a configuration identical with the original one.

The transformation of coordinates, resulting in identical arrangement of the atomic nuclei in a molecule, is called symmetry operation. The geometrical loci of the points that are caused by the symmetry operation to occupy positions identical with those of atomic nuclei in space are known as symmetry elements (Table 2).

TABLE 2. Conventional Symbols of Symmetry Operations and Elements

Symmetry element	Symbol	Symmetry operation	Symbol
Plane	σ	Reflection in a plane	$\hat{S}(\sigma)$
Rotational axis	C_n	Rotation through angle $2\pi/n$	$\hat{S}(C_n)$
Centre of symmetry	i	Reflection in a point	$\hat{S}(i)$
Rotation-reflection axis	S_n	Rotation about the axis and reflection in a plane normal to the axis	$\hat{S}(S_n)$

The principal axis of symmetry is the rotational axis having the highest order n . By convention, the symmetry plane in which the highest-order axis lies is denoted by the symbol σ_v , whereas the symmetry plane normal to the principal axis has been assigned the symbol σ_h .

In addition to the symmetry elements and operations listed in Table 2 mention should be made of the identity transformation E . It is equivalent to a situation in which a system of equilibrium configuration of atomic nuclei has not undergone any transformation at all.

A combination of several symmetry operations is usually written as a "product"* of the corresponding symmetry element symbols. The symbol of a symmetry operation performed later is written to the left of the operator \hat{S} of the previously performed operation.

Every molecule may be involved in a number of symmetry operations transforming it to a state identical with the one before the transformation. A complete set of such symmetry operations represents a symmetry group. The number of symmetry operations

*Here and in what follows the notion "product" has nothing to do with multiplication in the mathematical sense.

within a group is referred to as a group order. A group of operations, say a, b, c, \dots , is then defined as a set satisfying the following conditions: (1) the product of two operations in a group is equivalent to an operation in the same group ($ab = c$), (2) the system contains an identity operation E ($aE = Ea = a$), (3) corresponding to each operation is an inverse one which is an operation belonging to the same group ($aa^{-1} = a^{-1}a = E$), and (4) a product of several operations possesses the property of associativity: $a(bc) = (ab)c$.

All of the above symmetry operations leave at least one point in space unaltered. The set of symmetry operations leaving at least one point unaltered is termed point group. The number of possible point groups is limited. Any molecule must belong only to one of these point groups. All point groups fall under the following three main categories: (1) lowest symmetry groups containing only two-fold axes of symmetry and symmetry planes, (2) medium symmetry groups with only one axis of no less than three-fold symmetry, and (3) highest symmetry groups with several axes of no less than three-fold symmetry. Each point group has its own rather definite set of symmetry elements and operations. Table 3 lists point groups, their symbols, and all symmetry operations constituting a group.

TABLE 3. Point Symmetry Groups

Point group	Symmetry operations and elements	Point group	Symmetry operations and elements
C_1	E	D_{2h}	$E, 3C_2, 3\sigma, i$
C_2	E, C_2	D_{3h}	$E, C_3, 3C_2, 3\sigma_v, \sigma_h$
C_{2v}	$E, C_2, 2\sigma_v$	D_{4h}	$E, C_4, 4C_2, 4\sigma_v, \sigma_h, C_2, S_4, i$
C_{3v}	$E, C_3, 3\sigma_v$	D_{6h}	$E, C_6, 6C_2, 6\sigma_v, \sigma_h, C_2, C_3, S_6, i$
$C_{\infty v}$	$E, C_{\infty}, \infty\sigma_v$	$D_{\infty h}$	$E, C_{\infty}, \infty C_2, \infty\sigma_v, \sigma_h, i$
C_{2h}	E, C_2, σ_h, i	T_d	$E, 3C_2, 4C_3, 6\sigma, 3S_4$
D_{2d}	$E, 3C_2, S_4, 2\sigma_d$	O_h	$E, 3C_4, 4C_3, 3S_4, 3C_2, 6C_2, 3\sigma, 4S_6$
D_{3d}	$E, C_3, 3C_2, S_6, i, 3\sigma_d$		

Table 3 is instrumental in identifying all symmetry elements inherent in a molecule in a state of equilibrium.

Exercises

1. Write the MO of the molecule O_2 and ions O_2^+ and O_2^- . Arrange these particles in the order of increasing equilibrium internuclear distance, proceeding from the bond order.

Solution. Write the electronic configurations and determine the bond order:

$$\text{O}_2 (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\pi_{2p_y}^*) (\pi_{2p_z}^*)^2$$

$$u = \frac{1}{2} (10 - 6) = 2$$

$$\text{O}_2^+ (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\pi_{2p_y}^*)$$

$$u = \frac{1}{2} (10 - 5) = 2.5$$

$$\text{O}_2^- (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\pi_{2p_y}^*)^2 (\pi_{2p_z}^*)$$

$$u = \frac{1}{2} (10 - 7) = 1.5$$

The bond order values suggest that the internuclear distances will increase in the series: O_2^+ , O_2 , O_2^- .

2. Proceeding from the electronic structures of BN, BO, and CO, arrange these particles in the order of increasing equilibrium inter-nuclear distance.

Solution. Write the electronic configurations in these particles and calculate the bond order:

$$\text{BN} (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\sigma_{2p_x})$$

$$u = \frac{1}{2} (8 - 4) = 2$$

$$\text{BO} (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\sigma_{2p_x})$$

$$u = \frac{1}{2} (9 - 4) = 2.5$$

$$\text{CO} (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\sigma_{2p_x})^2$$

$$u = \frac{1}{2} (10 - 4) = 3$$

The bond order values suggest that the equilibrium internuclear distances will increase in the series: CO, BO, BN.

3. Determine the equilibrium geometrical configuration of the molecule BeH_2 in terms of the MO theory. Define the point symmetry group.

Solution. The molecule BeH_2 contains a total of four electrons participating in σ -bonding. There are two bonding electron pairs. The molecule lacks unshared electron pairs. As can be inferred from

the diagram in Fig. 5, the equilibrium geometrical configuration of the molecule BeH_2 is linear. The molecule belongs to the point symmetry group $C_{\infty v}$.

4. A point L has coordinates x , y , and z . Write the transformation equations for the symmetry operation $\hat{S}(\sigma_z)$.

Solution. The symmetry operation $\hat{S}(\sigma_z)$ is a reflection in the plane xy . Plot the point before the symmetry operation (L) and after (L'), as in Fig. 6. The transformation equations will be

$$\hat{S}(\sigma_z) x = x; \quad \hat{S}(\sigma_z) y = y; \quad \hat{S}(\sigma_z) z = -z$$

5. A point has coordinates x , y , and z . Write the transformation equations for the symmetry operation $\hat{S}(\sigma_x)$.

Solution. The symmetry operation $\hat{S}(\sigma_x)$ (see Table 2) is a reflection of the point in the plane yz in Fig. 6. The point L will become L'' after the reflection operation. Hence the transformation equations are:

$$\hat{S}(\sigma_x) x = -x; \quad \hat{S}(\sigma_x) y = y,$$

$$\hat{S}(\sigma_x) z = z$$

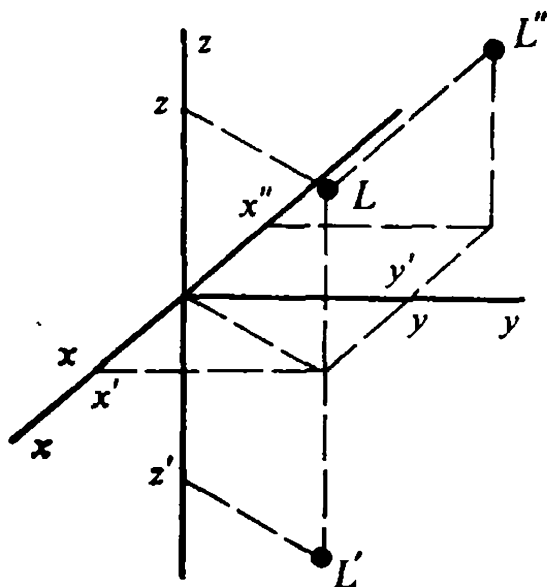


Fig. 6. $\hat{S}(\sigma_z)$ Transformation of a point in a plane

6. Analyse the symmetry elements and operations for the molecule NH_3 .

Solution. The ammonia molecule NH_3 has the structure of a trihedral pyramid with the nitrogen nucleus at its vertex. The three-fold axis of symmetry C_3 passes through the nucleus of the nitrogen atom, and there are three symmetry planes

σ_v . Consequently, according to Table 3, the molecule NH_3 belongs to the point group C_{3v} .

7. Using the molecule NH_3 as an example, check whether the first condition of a group, whereby the product of two symmetry elements is a symmetry element, is met.

Solution. Write all possible products of symmetry operations for NH_3 in the form of a matrix of products. To this end, the first line and the first column must include all symbols of the symmetry elements of the molecule NH_3 . The intersection of the line and column will contain the symbol of the corresponding product of the symmetry element in the first column by that in the first line.

C_3	E	C_3	C_3^2	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$
E	E	C_3	C_3^2	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$
C_3	C_3	C_3^2	E	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$	$\sigma_v^{(1)}$
C_3^2	C_3^2	E	C_3	$\sigma_v^{(3)}$	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$
$\sigma_v^{(1)}$	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$	E	C_3^2	C_3
$\sigma_v^{(2)}$	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$	$\sigma_v^{(1)}$	C_3	E	C_3^2
$\sigma_v^{(3)}$	$\sigma_v^{(3)}$	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$	C_3^2	C_3	E

The symmetry elements in the second line and in the second column do not differ from those in the first line and in the first column, respectively, because they are essentially a product by the identity element E . To form the third column first mentally perform the operation in the first column, then the operation in the first line. For example, $C_3\sigma_v^{(1)} = \sigma_v^{(2)}$. The matrix shows that all products of two elements represent a symmetry element.

Problems

1. Determine the equilibrium geometrical configuration of the molecule CO_2 in terms of the MO theory. Define its point symmetry group and enumerate the symmetry elements.

2. Determine the equilibrium geometrical configuration of the ion NO_3^- . Define the point symmetry group and enumerate the symmetry elements.

3. Determine the equilibrium geometrical configuration of the molecule NH_3 . Define the point symmetry group and enumerate the symmetry elements.

4. Determine the equilibrium geometrical configuration of the particle PF_5 . Define the point symmetry group and enumerate the symmetry elements.

5. Determine the equilibrium geometrical configuration of IF_5 . Define the point symmetry group and enumerate the symmetry elements.

6. What is the order of the symmetry axis passing through the two carbon atoms in the para position in the benzene molecule?

7. What is the order of the symmetry axis passing through the centre of gravity of the benzene molecule at a right angle to its plane?

8. Write the coordinate transformation equations for the symmetry operations $\hat{S}(C_n) x$, $\hat{S}(C_n) y$, and $\hat{S}(C_n) z$.

9. Write the coordinate transformation equations for the symmetry operations $\hat{S}(S_n) x$, $\hat{S}(S_n) y$, and $\hat{S}(S_n) z$; z is a rotation reflection axis.

Multivariant Problem

Define the point symmetry group, determine the equilibrium geometrical configuration, and enumerate the symmetry elements for compound A.

Variant	Compound A	Variant	Compound A	Variant	Compound A
1	H ₂ O	10	CO ₃ ²⁻	18	NF ₃
2	PtCl ₄ ²⁻	11	C ₂ O ₄	19	N ₂ O
3	NH ₃	12	SO ₂	20	O ₃
4	SiHF ₃	13	SO ₃	21	PI ₃
5	SiCl ₄	14	PCl ₃	22	SO ₄ ²⁻
6	HCN	15	C ₆ H ₆	23	SbCl ₃
7	SiH ₃ F	16	SbF ₃	24	CH ₄
8	SiH ₄	17	NCIO ₂	25	CHCl ₃
9	CH≡CH				

CHAPTER 3

Rotation and Rotational Spectra of Diatomic Molecules

Basic Equations and Symbols

The rotational energy of a molecule is determined from the equation

$$\varepsilon_{\text{rot}} = \frac{h^2}{8\pi^2 I} j(j+1) = \frac{h^2}{2I} j(j+1) \quad (3.1)$$

where I is the moment of inertia, kg m²; h is Planck's constant; and j is the rotational quantum number. If it is assumed that the parameters of a molecule during rotation remain constant ($r_e = \text{const}$ and $I = \text{const}$), Eq. (3.1) can be written as

$$\varepsilon_{\text{rot}} = B_e j(j+1) \quad (3.2)$$

where $B_e = h^2/8\pi^2 I$ is the rotational constant, J.

A change in the rotational energy of a molecule will be

$$\Delta \epsilon_{\text{rot}} = \epsilon'_{\text{rot}} - \epsilon''_{\text{rot}} = \frac{h^2}{8\pi^2 I} [j' (j' + 1) - j'' (j'' + 1)] \quad (3.3)$$

where ϵ'_{rot} is the rotational energy in the final state of the system, and ϵ''_{rot} is the rotational energy in the initial state. Since according to the Pauli-Fermi principle $\Delta j = \pm 1$, in the absorption spectrum $\Delta j = +1$ and $j' - j'' = 1$, and Eq. (3.3) takes the form

$$\Delta \epsilon_{\text{rot}} = \frac{h^2}{4\pi^2 I} (j + 1) \quad (3.4)$$

$$\Delta \epsilon_{\text{rot}} = hc\tilde{\nu} \quad (3.5)$$

where c is the velocity of light, and $\tilde{\nu}$ is the wave number of an absorbed light quantum;

$$\tilde{\nu} = \frac{\Delta \epsilon_{\text{rot}}}{hc} = \frac{h}{4\pi^2 I c} (j + 1) \quad (3.6)$$

or, for a rigid rotator,

$$\tilde{\nu} = B'_e (j + 1) \quad (3.7)$$

$B'_e = \frac{h}{4\pi^2 I c}$ being the rotational constant, m^{-1} . If the constants are substituted, then

$$B'_e = \frac{5.5981 \times 10^{-44}}{I} \quad (3.8)$$

The molecule's moment of inertia in the general expression will be

$$I = \sum_1^i m_i r_i^2 \quad (3.9)$$

For asymmetrical diatomic molecules

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (3.10)$$

In the case of free rotation of the molecule, $m_1 r_1 = m_2 r_2$, then

$$I = \mu r_e^2 \quad (3.11)$$

where μ is the reduced mass;

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{a_1 a_2}{a_1 + a_2} \frac{m_C}{12} \quad (3.12)$$

where a_i stands for atomic masses; m_C is the mass of the carbon atom, kg; $m_C/12 = 1.6604 \times 10^{-27}$ kg;

$$r_e = \sqrt{\frac{1}{\mu}} = \sqrt{\frac{h}{4\pi^2 B'_e c \mu}} = \frac{1}{2\pi} \sqrt{\frac{h}{B'_e c \mu}} \quad (3.13)$$

The difference between the wave numbers of adjacent lines in the rotational absorption spectrum is

$$\Delta\tilde{\nu} = \tilde{\nu}'_1 - \tilde{\nu}''_2 = B'_e \quad (3.14)$$

The absorption of light quanta by a molecule of a substance is possible only when the molecule has a constant electric dipole moment.

The rotational energy levels are degenerate. The degeneracy g_j is determined from the equation

$$g_j = 2j + 1 \quad (3.15)$$

Exercises

1. In the far IR region $^1\text{H}^{35}\text{Cl}$ absorbs radiation with the following wave numbers:

Line No.	1	2	3	4	5	6	7
$\tilde{\nu}$, m^{-1}	8538.4	10673.0	12807.6	14942.2	17076.8	19211.4	21346.6

Find the mean value of the moment of inertia and the internuclear distance.

Solution. Given the above wave numbers of the absorption lines associated with the change in rotational energy, determine the value of $\Delta\tilde{\nu}_{\text{av}}$. To this end, determine the difference between the wave numbers of adjacent lines and the mean value of $\Delta\tilde{\nu}_{\text{av}}$ will be 2134.6 m^{-1} . Then, Eqs. (3.14) and (3.8) will give the value of the moment of inertia:

$$I = \frac{5.5981 \times 10^{-44}}{2134.6} = 2.6226 \times 10^{-47} \text{ kg m}^2$$

The equilibrium internuclear distance is calculated using Eq. (3.13); to do this we must know the reduced mass which is derived from Eq. (3.12):

$$\mu = \frac{1 \times 35}{1 + 35} 1.6604 \times 10^{-27} = 1.6143 \times 10^{-27} \text{ kg}$$

$$r_e = \sqrt{\frac{2.6226 \times 10^{-47}}{1.6143 \times 10^{-27}}} = 1.2746 \times 10^{-10} \text{ m}$$

2. Calculate the wave number of the line in the rotational absorption spectrum of $^{19}\text{F}^{79}\text{Br}$, which corresponds to the transition of the molecule from the level $j = 1$ to the rotational quantum level $j = 2$, provided the equilibrium internuclear distance r_e is $1.7555 \times 10^{-10} \text{ m}$.

Solution. The wave number of the absorption line is determined using Eq. (3.6). For this purpose the molecule's moment of inertia is to be calculated. Determine the reduced mass from Eq. (3.12)

and the moment of inertia from Eq. (3.11):

$$\mu = \frac{19 \times 79}{19 + 79} 1.6604 \times 10^{-27} = 15.3 \times 1.6604 \times 10^{-27} = 25.4 \times 10^{-27} \text{ kg}$$

$$I = 25.4 \times 10^{-27} (1.7555 \times 10^{-10})^2 = 78.355 \times 10^{-47} \text{ kg m}^2$$

Then,

$$\tilde{\nu} = \frac{6.6256 \times 10^{-34} (1 + 1)}{4 \times 3.14^2 \times 3 \times 10^8 \times 78.355 \times 10^{-47}} = 0.714 \times 10^2 \times 2 = 1.428 \times 10^2 \text{ m}^{-1}$$

3. Determine the rotational energy of $^{19}\text{F}^{79}\text{Br}$ on the rotational quantum level $j = 1$ if the equilibrium internuclear distance r_e is $1.7555 \times 10^{-10} \text{ m}$.

Solution. Knowing the internuclear distance and having determined the reduced mass of the molecule, find the moment of inertia I . Hence, according to Eq. (3.1), the rotational energy will be

$$\varepsilon_1 = \frac{(6.6256 \times 10^{-34})^2}{8\pi^2 \times 78.355 \times 10^{-47}} 1 (1 + 1)$$

$$= 0.07096 \times 10^{-22} \times 1 \times 2 = 0.1419 \times 10^{-22} \text{ J}$$

4. What is the difference between the wave numbers of absorption lines in the rotational spectra of $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ if the line corresponds to transition of the molecule from the rotational quantum level $j = 6$ to $j = 7$? The equilibrium internuclear distance in both molecules is the same and equal to $1.2746 \times 10^{-10} \text{ m}$.

Solution. Determine the moments of inertia of the molecules $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$:

$$^1\text{H}^{35}\text{Cl } I = \frac{1 \times 35}{1 + 35} 1.6604 \times 10^{-27} (1.2746 \times 10^{-10})^2$$

$$= 2.6226 \times 10^{-47} \text{ kg m}^2$$

$$^1\text{H}^{37}\text{Cl } I = \frac{1 \times 37}{1 + 37} 1.6604 \times 10^{-27} (1.2746 \times 10^{-10})^2$$

$$= 2.6265 \times 10^{-47} \text{ kg m}^2$$

$$\text{for } ^1\text{H}^{35}\text{Cl } \tilde{\nu} = \frac{5.5981 \times 10^{-44}}{2.6226 \times 10^{-47}} 6 \times 7 = 89.6516 \times 10^3 \text{ m}^{-1}$$

$$\text{for } ^1\text{H}^{37}\text{Cl } \tilde{\nu} = \frac{5.5981 \times 10^{-44}}{2.6265 \times 10^{-47}} 6 \times 7 = 89.5184 \times 10^3 \text{ m}^{-1}$$

The absorption line of $^1\text{H}^{35}\text{Cl}$ is shifted with respect to the line of $^1\text{H}^{37}\text{Cl}$ towards smaller wave numbers by 133.15 m^{-1} .

Problems

1. Given the equilibrium internuclear distance in the molecule $^1\text{H}^{127}\text{I}$ (use one of the standard handbooks), calculate its moment of inertia.

2. Determine the rotational energy of the molecule $^1\text{H}^{127}\text{I}$ on the first ten rotational quantum levels and the wave numbers of the first nine lines in the rotational absorption spectrum, if the mole-

cule's moment of inertia I is 4.295×10^{-47} kg m². The molecule is a rigid rotator.

3. In the far IR region of the rotational absorption spectrum of a substance HX several absorption lines are observed with the following wave numbers (m⁻¹): 13649.4, 15355.6, and 17061.8. The equilibrium internuclear distance $r_e = 1.4146 \times 10^{-10}$ m. Determine the atomic mass of X.

4. Compare the rotational energies of HF molecules on the first ten rotational quantum levels with the mean kinetic energy of the molecules' translational motion at the following temperatures (K): 300, 500, and 1000. The value of the moment of inertia is given in the handbook.

5. Determine the wave numbers of the first ten lines in the far IR region of the absorption spectrum of ¹H¹⁹F. The molecule's moment of inertia is given in the handbook.

6*. Determine the ratio N_j/N_0 (N_j and N_0 standing for the number of molecules on the j th and zeroth rotational quantum levels of ¹H¹⁹F) on the first ten rotational quantum levels at 300 K.

7*. Determine $\sum_{j=0}^9 \frac{N_j}{N_0}$ and, ignoring the number of ¹H¹⁹F molecules occupying the rotational levels $j > 9$ at 300 K, calculate the number of molecules on the first ten rotational quantum levels, provided 1 mole of ¹H¹⁹F is taken.

8*. Given the results of solution of Problems 4, 5, and 7, draw the energy levels, transitions of molecules during absorption of electromagnetic radiation, and the absorption spectrum, taking into account that the probability of absorption is independent of the energy of the quantum level from which the transfer occurs.

9*. The following lines have been identified in the spectrum of ¹²C¹⁶O, taken with the aid of a high-resolution instrument:

j	$\tilde{\nu}$, cm ⁻¹	j	$\tilde{\nu}$, cm ⁻¹	j	$\tilde{\nu}$, cm ⁻¹
0	3.845	10	42.263	21	84.330
1	7.690	11	46.098	22	88.138
2	11.534	12	49.939	23	91.943
3	15.379	13	53.763	24	95.744
4	19.222	14	57.593	25	99.541
5	23.065	15	61.420	26	103.334
6	26.907	16	65.245	27	107.124
7	30.748	17	69.068	28	110.909
8	34.588	18	72.888	29	114.690
9	38.426	19	76.705	30	118.467
		20	80.519		

Find the mean value of the moment of inertia and the equilibrium internuclear distance in the molecule $^{12}\text{C}^{16}\text{O}$.

10. Proceeding from the data tabulated in Problem 9, determine the rotational energy (in J) of the molecule $^{12}\text{C}^{16}\text{O}$ on the rotational quantum level $j = 30$.

11*. Proceeding from the data tabulated in Problem 9, determine the change in the internuclear distance in the molecule $^{12}\text{C}^{16}\text{O}$ as it is transferred from the zeroth to the 30th rotational quantum level. Demonstrate that the molecule $^{12}\text{C}^{16}\text{O}$ is not a rigid rotator.

12. Determine the difference between the wave numbers of absorption lines in the rotational spectrum of the molecules $^1\text{H}^{35}\text{Cl}$ and $^2\text{H}^{35}\text{Cl}$ during their transition from the rotational quantum level $j = 6$ to $j = 7$. The equilibrium internuclear distance is the same in both molecules and equals 1.2746×10^{-10} m.

Multivariant Problems

1. Calculate the moment of inertia and the equilibrium internuclear distance in molecule A from the difference between the wave numbers of adjacent absorption lines in the far IR region.

Variant	Molecule A	$\Delta\tilde{\nu}$, cm ⁻¹	Variant	Molecule A	$\Delta\tilde{\nu}$, cm ⁻¹
1	$^1\text{H}^{35}\text{Cl}$	21.35	14	$^2\text{H}^{81}\text{Br}$	8.64
2	$^2\text{H}^{35}\text{Cl}$	10.97	15	$^3\text{H}^{81}\text{Br}$	5.83
3	$^3\text{H}^{35}\text{Cl}$	7.51	16	$^{35}\text{Cl}^{19}\text{F}$	1.03
4	$^1\text{H}^{37}\text{Cl}$	21.32	17	$^{37}\text{Cl}^{19}\text{F}$	1.01
5	$^2\text{H}^{37}\text{Cl}$	10.94	18	$^{35}\text{Cl}^{79}\text{Br}$	0.195
6	$^3\text{H}^{37}\text{Cl}$	7.48	19	$^{35}\text{Cl}^{81}\text{Br}$	0.194
7	$^1\text{H}^{79}\text{Br}$	17.06	20	$^{37}\text{Cl}^{79}\text{Br}$	0.188
8	$^2\text{H}^{79}\text{Br}$	8.64	21	$^{37}\text{Cl}^{81}\text{Br}$	0.187
9	$^3\text{H}^{79}\text{Br}$	5.83	22	$^1\text{H}^{127}\text{I}$	13.13
10	$^1\text{H}^{19}\text{F}$	42.22	23	$^2\text{H}^{127}\text{I}$	6.61
11	$^2\text{H}^{19}\text{F}$	42.17	24	$^3\text{H}^{127}\text{I}$	4.44
12	$^3\text{H}^{19}\text{F}$	15.48	25	$^{12}\text{C}^{14}\text{N}$	3.80
13	$^1\text{H}^{81}\text{Br}$	17.06			

2. Given the equilibrium internuclear distance in molecule A, calculate the wave numbers of the first ten lines in the rotational absorption spectrum, assuming that the molecule is a rigid rotator.

Variant	Molecule A	$r_e \times 10^{10}, \text{ m}$	Variant	Molecule A	$r_e \times 10^{10}, \text{ m}$
1	$^{12}\text{C}^1\text{H}$	1.120	14	$^{32}\text{S}^1\text{H}$	1.341
2	$^{12}\text{C}^{16}\text{O}$	1.128	15	$^{32}\text{S}^{16}\text{O}$	1.481
3	$^{12}\text{C}^{19}\text{F}$	1.267	16	$^{12}\text{C}^2\text{H}$	1.120
4	$^{12}\text{C}^{35}\text{Cl}$	1.645	17	$^{12}\text{C}^{37}\text{Cl}$	1.645
5	$^{12}\text{C}^{31}\text{P}$	1.558	18	$^{28}\text{Si}^2\text{H}$	1.521
6	$^{28}\text{Si}^1\text{H}$	1.521	19	$^{28}\text{Si}^{37}\text{Cl}$	2.058
7	$^{28}\text{Si}^{16}\text{O}$	1.509	20	$^{14}\text{N}^2\text{H}$	1.038
8	$^{28}\text{Si}^{19}\text{F}$	1.600	21	$^{16}\text{O}^3\text{H}$	0.971
9	$^{28}\text{Si}^{35}\text{Cl}$	2.058	22	$^{32}\text{S}^2\text{H}$	1.341
10	$^{14}\text{N}^1\text{H}$	1.038	23	$^{12}\text{C}^3\text{H}$	1.120
11	$^{14}\text{N}^{16}\text{O}$	1.151	24	$^{28}\text{Si}^3\text{H}$	1.521
12	$^{16}\text{O}^1\text{H}$	0.971	25	$^{32}\text{S}^3\text{H}$	1.341
13	$^{16}\text{O}^2\text{H}$	0.971			

CHAPTER 4

Rotation and Rotational Spectra of Polyatomic Molecules

Basic Equations and Symbols

The moments of inertia of a molecule rotation about the principal axes passing through its centre of gravity will be:

$$I_x = \sum_i m_i r_{ix}^2, \quad I_y = \sum_i m_i r_{iy}^2, \quad I_z = \sum_i m_i r_{iz}^2 \quad (4.1)$$

where m_i stands for masses of atomic nuclei, and r_{ix} , r_{iy} , and r_{iz} are the equilibrium distances from the atomic nuclei to the axes of rotation. Taken as the origin of coordinates is the molecule's centre of gravity whose ordinates can be determined from the equations:

$$\sum_i m_i r_{ix} = 0, \quad \sum_i m_i r_{iy} = 0, \quad \sum_i m_i r_{iz} = 0 \quad (4.2)$$

Linear polyatomic molecules have two degrees of freedom of rotation about axes normal to that of the molecule. Nonlinear polyatomic molecules have three degrees of freedom of rotation.

Distinction is made between three types of molecules: (1) spherical top, $I_x = I_y = I_z$; molecules of this type have several axes of symmetry of the order $n \geq 3$; (2) asymmetric top, $I_x \neq I_y \neq I_z$; molecules of this type lack axes of symmetry of the order $n \geq 3$; (3) symmetric top with two of the three moments of inertia being equal to each other: $I_x = I_y \neq I_z$ or $I_x \neq I_y = I_z$. A common trait

of the rotational energy levels of polyatomic molecules is the values of the quantum numbers j and m_j :

$$\epsilon_{\text{rot}} = \frac{M_{p_x}^2}{2I_x} + \frac{M_{p_y}^2}{2I_y} + \frac{M_{p_z}^2}{2I_z} \quad (4.3)$$

where M_{p_x} , M_{p_y} , and M_{p_z} are angular momenta. At the same time, the projection of the angular momentum on the axis of the fixed coordinate system is quantized:

$$M_{p_x} = \frac{h}{2\pi} m_j \quad (4.4)$$

where m_j is a quantum number assuming integer values from $-j$ to $+j$, including zero. Consequently, m_j assumes the value $2j + 1$. For a spherical top with $I_x = I_y = I_z$:

$$\epsilon_{\text{rot}} = \frac{1}{2I} (M_{p_x}^2 + M_{p_y}^2 + M_{p_z}^2) = \frac{M_p^2}{2I} \quad (4.5)$$

$$M_p = 2\epsilon_{\text{rot}} I = \frac{h}{2\pi} \sqrt{j(j+1)} \quad (4.6)$$

The quantized values of energy will be the same as in diatomic molecules (see Eq. (3.1)). However, polyatomic molecules of the spherical top type have three degrees of freedom, which means that for the rotation to be represented as completely as possible another quantum number k is needed in addition to j and m_j . The quantum number k determines the projection of the angular momentum on one of the mobile axes rotating together with the molecule:

$$M_{p_k} = (h/2\pi) k \quad (4.7)$$

The quantum number k assumes values from $-j$ to $+j$, including zero. Hence, the degeneracy of the level will be

$$g_j = (2j + 1) (2j + 1) = (2j + 1)^2 \quad (4.8)$$

The distribution of molecules among the rotational quantum levels is:

$$N_j = (2j + 1)^2 N_0 e^{-\frac{h^2}{8\pi^2 I} j(j+1) \frac{1}{kT}} \quad (4.9)$$

In the case of a prolate symmetric top with $I_x < I_y = I_z$, the relationship between the rotational constants will be $A > B = C$. From Eq. (4.5) and from the ratio of moments of inertia for a prolate symmetric top the rotational energy will take the form

$$\begin{aligned} \epsilon_{\text{rot}} &= \frac{1}{2I_x} M_{p_x}^2 + \frac{1}{2I_y} (M_{p_y}^2 + M_{p_z}^2) \\ &= \frac{1}{2} \left(\frac{1}{I_x} - \frac{1}{I_y} \right) M_{p_x}^2 + \frac{1}{2I_y} M_p^2 \end{aligned} \quad (4.10)$$

$$\epsilon_{jk} = \left(\frac{h^2}{8\pi^2 I_x} - \frac{h^2}{8\pi^2 I_y} \right) k^2 + \frac{h^2}{8\pi^2 I_y} j(j+1) \quad (4.11)$$

After transformation Eq. (4.11) takes the form

$$\varepsilon_{jk} = (A - B) k^2 + B j (j + 1) \quad (4.12)$$

In the case of an oblate symmetric top with $I_x = I_y < I_z$, the relationship between the rotational constants will be $A = B > C$. Accordingly,

$$\varepsilon_{jk} = (C - B) k^2 + B j (j + 1) \quad (4.13)$$

The second term in Eqs. (4.11) and (4.12) depends only on the rotational quantum number j . The first term depends on the square of the quantum number k determining the projection of the angular momentum on the principal axis of symmetry passing through the molecule's centre of gravity. Each energy level is degenerate $2(2j + 1)$ times, except for the zeroth level where $k = 0$ and the degeneracy is $(2j + 1)$ -fold. When quanta of electromagnetic radiation are absorbed, molecular transitions $\Delta j = +1$ and $\Delta k = 0$ are observed in the rotational spectrum.

Exercises

1. Find the internuclear distance $r_{e_{C-O}}$ in the molecule CO_2 , if the moment of inertia I is 71.758×10^{-47} kg m². The molecule CO_2 has the $D_{\infty h}$ symmetry.

Solution. Since the molecule CO_2 is linear, there are only two degrees of freedom of rotation about an axis normal to that of the molecule. Both moments of inertia are the same. Rotation of the molecule about its own axis is impossible because the moment of inertia of such rotation is zero and, consequently, the rotational energy according to Eq. (3.1) is infinitely great. Find the equilibrium internuclear distance using Eq. (4.1):

$$I = \sum_1^2 m_i r_i^2 = 2 \times 16 \times 1.6604 \times 10^{-27} r_{e_{C-O}}^2$$

$$r_{e_{C-O}} = \sqrt{\frac{71.758 \times 10^{-47}}{2 \times 16 \times 1.6604 \times 10^{-27}}} = 1.1621 \times 10^{-10} \text{ m}$$

2. Determine the moment of inertia and the rotational constant of the molecule OCS, if the microwave region of the absorption spectrum features the following absorption maxima (m⁻¹): 81.143, 121.714, 126.686, and 202.886. The molecule OCS is linear, symmetry type: $C_{\infty v}$.

Solution. Determine the mean difference between the wave numbers of adjacent lines in the absorption spectrum (m⁻¹): $\Delta \tilde{\nu}_1 = 40.571$, $\Delta \tilde{\nu}_2 = 40.572$, $\Delta \tilde{\nu}_3 = 40.600$, $\Delta \tilde{\nu}_{av} = 40.581$. Since the molecule OCS is linear, there are only two degrees of freedom of rota-

tion. Both moments of inertia are equal. Find the moment of inertia using the equation

$$I = \frac{h}{4\pi^2 c \Delta \tilde{\nu}}, \quad I = \frac{5.5981 \times 10^{-44}}{40.581} = 137.949 \times 10^{-47} \text{ kg m}^2$$

The rotational constant will be

$$B'_e = \frac{h}{4\pi^2 c I} = \Delta \tilde{\nu} = 40.581 \text{ m}^{-1}$$

3. Find the product of the moments of inertia, $I_A I_B I_C$, of the water molecule, if the equilibrium internuclear distances are $r_{\text{O-H}} = 0.957 \times 10^{-10} \text{ m}$ and the equilibrium HOH angle is $104^\circ 31'$. The molecule H_2O has the C_{2v} symmetry.

Solution. Assume that the origin of coordinates is the molecule's centre of gravity which will be determined from Eqs. (4.2). Then, the moments of inertia will be I_x , I_y , and I_z and determined from Eqs. (4.1). The product of the principal moments of inertia of the molecule can be calculated using the secular equation

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} - I_{xy} - I_{xz} \\ -I_{xy} + I_{yy} - I_{yz} \\ -I_{xz} - I_{yz} + I_{zz} \end{vmatrix}$$

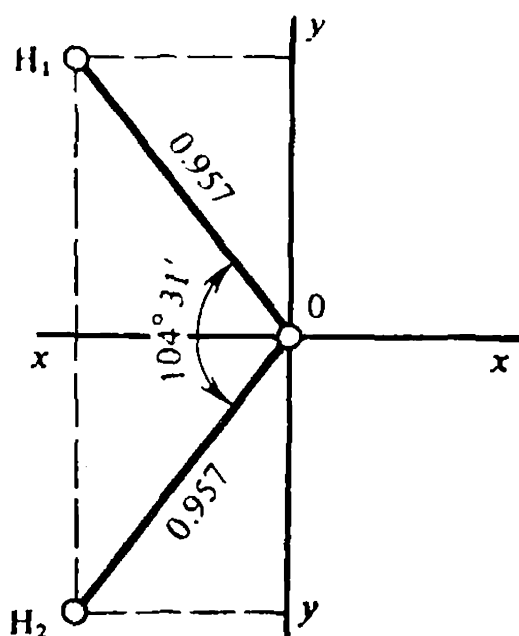


Fig. 7. Equilibrium geometrical configuration of the water molecule

To calculate the values of I_{ij} use the following equations:

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) - \frac{1}{M} \left(\sum m_i y_i \right)^2 - \frac{1}{M} \left(\sum m_i z_i \right)^2$$

$$I_{yy} = \sum m_i (x_i^2 + z_i^2) - \frac{1}{M} \left(\sum m_i x_i \right)^2 - \frac{1}{M} \left(\sum m_i z_i \right)^2$$

$$I_{zz} = \sum m_i (x_i^2 + y_i^2) - \frac{1}{M} \left(\sum m_i x_i \right)^2 - \frac{1}{M} \left(\sum m_i y_i \right)^2$$

$$I_{xy} = \sum m_i x_i y_i - \frac{1}{M} \left(\sum m_i x_i \right) \left(\sum m_i y_i \right)$$

$$I_{xz} = \sum m_i x_i z_i - \frac{1}{M} \left(\sum m_i x_i \right) \left(\sum m_i z_i \right)$$

$$I_{yz} = \sum m_i y_i z_i - \frac{1}{M} \left(\sum m_i y_i \right) \left(\sum m_i z_i \right)$$

where $M = \sum m_i$. The solution of the third-order secular equation will be

$$I_A I_B I_C = I_{xx} (I_{yy} I_{zz} - I_{yz} I_{yz}) - I_{xy} (I_{xy} I_{zz} - I_{yz} I_{xz}) - I_{xz} (I_{xy} I_{yz} + I_{yy} I_{xz})$$

The solution should better be in a tabular form. The water molecule, the coordinates of the atomic nuclei, the equilibrium internuclear distances, the equilibrium angle, and the coordinate axes are given in Fig. 7.

Atom	$m \times 10^{26}$, kg	$x \times 10^{10}$, m	$y \times 10^{10}$, m	$z \times 10^{10}$, m
O	2.656	0	0	0
H ₁	0.166	−0.586	0.757	0
H ₂	0.166	−0.586	−0.757	0
	$\sum m_i = 2.988 \times 10^{-26}$ kg			

Atom	O	H ₁	H ₂	Σ
$x^2 \times 10^{20}$	0	0.343	0.343	
$y^2 \times 10^{20}$	0	0.573	0.573	
$xy \times 10^{20}$	0	−0.444	0.444	
$mx \times 10^{36}$	0	−0.097	−0.097	−0.194
$my \times 10^{36}$	0	0.126	−0.126	0
$mxy \times 10^{46}$	0	−0.074	0.074	0
$m(x^2 + y^2) \times 10^{46}$	0	0.152	0.152	0.304
$mx^2 \times 10^{46}$	0	0.057	0.057	0.114
$my^2 \times 10^{46}$	0	0.095	0.095	0.190

$$I_{xx} = 0.190 \times 10^{-46}$$

$$I_{yy} = 0.114 \times 10^{-46} - \frac{0.038}{2.988} 10^{-46} = 0.101 \times 10^{-46}$$

$$I_{zz} = 0.304 \times 10^{-46} - 0.038 \frac{1}{2.988} 10^{-46} = 0.291 \times 10^{-46}$$

$$I_{xy} = 0, \quad I_{xz} = 0, \quad \text{and} \quad I_{yz} = 0. \quad \text{Then,}$$

$$I_A I_B I_C = 0.190 \times 10^{-46} \times 0.101 \times 10^{-46} \times 0.291 \times 10^{-46} = 55.84 \times 10^{-142} \text{ (kg m}^2\text{)}^3$$

Problems

1. Find the equilibrium distance between the nuclei of the atoms C and S in the molecule CS_2 from the moment of inertia $I = 94.507 \times 10^{-47} \text{ kg m}^2$. The symmetry of the molecule CS_2 is $D_{\infty h}$.

2. The mean difference between the wave numbers of adjacent lines in the rotational absorption spectrum of HCN is $2.977 \times 10^2 \text{ m}^{-1}$. Determine the moment of inertia and the rotational constant B' (m^{-1}).

3*. Determine the product of the moments of inertia, $I_A I_B I_C$, of the molecule SO_2 from the equilibrium internuclear distance $r_{\text{S-O}} = 1.432 \times 10^{-10} \text{ m}$ and the equilibrium OSO angle equal to $119^\circ 21'$. The symmetry of the molecule SO_2 is C_{2v} .

4*. Determine the product of the moments of inertia, $I_A I_B I_C$, of the molecule $\text{CH}^{35}\text{Cl}_3$ if the equilibrium internuclear distances are $r_{\text{C-H}} = 1.073 \times 10^{-10} \text{ m}$ and $r_{\text{C-Cl}} = 1.763 \times 10^{-10} \text{ m}$ and the ClCH angle is $108^\circ 32'$. The symmetry of the molecule CHCl_3 is C_{3v} .

5. From the moments of inertia of the water molecule $I_A = 0.996 \times 10^{-47}$, $I_B = 1.908 \times 10^{-47}$, and $I_C = 2.981 \times 10^{-47} \text{ kg cm}^2$ determine the equilibrium internuclear distance $r_{\text{O-H}}$ and the HOH angle.

6. Prove that for nonlinear triatomic molecules $I_A \neq I_B \neq I_C$ and $I_A + I_B = I_C$.

7*. Determine the principal moments of inertia of the molecule $^{31}\text{P}^1\text{H}_3$ from the equilibrium internuclear distance $r_{\text{P-H}} = 1.4206 \times 10^{-10} \text{ m}$ and the HPH angle equal to $93^\circ 5'$. Find out whether the molecule PH_3 is an oblate or prolate symmetric top.

8*. Determine the energies of the first ten rotational quantum levels of the molecule $^{31}\text{P}^1\text{H}_3$ if the principal moments of inertia of the molecule are $I_A = I_B = 6.237 \times 10^{-47} \text{ kg m}^2$ and $I_C = 7.111 \times 10^{-47} \text{ kg m}^2$. Draw the energy levels to a conventional scale, using arrows to indicate the possible transitions during absorption of light quanta in the far IR region.

9. The moment of inertia of the molecule NH_3 about the principal axis of symmetry is $I = 1.085 \times 10^{-47} \text{ kg m}^2$. Define the ratio of the number of molecules on the rotational level $j = 5$ to that of molecules on the zeroth rotational quantum level at 1000 K.

10. Determine the principal moments of inertia and the product of the principal moments of inertia of the benzene molecule if $r_{\text{C-H}} = 1.084 \times 10^{-10} \text{ m}$ and $r_{\text{C-C}} = 1.397 \times 10^{-10} \text{ m}$. The benzene molecule is planar and has the D_{6h} symmetry.

Multivariant Problem

The molecule XY_4 has the T_d symmetry. Given the equilibrium internuclear distance X-Y: (1) determine the molecule's moment of inertia, (2) calculate the rotational constant B_e (in J) of the mole-

cule, (3) calculate its rotational energy on the rotational quantum level $j = 10$, (4) calculate the ratio of the number of molecules on the level $j = 10$ to that of molecules on the zeroth rotational quantum level at 300 K, (5*) calculate the rotational energies of the molecule XY_4 on the first twenty rotational quantum levels, (6*) calculate N_j/N_0 for the first twenty rotational quantum levels at 300 K, (7*) calculate $\sum \frac{N_j}{N_0}$ at 300 K, (8*) determine the number of molecules on the zeroth rotational quantum level if 1 mole of XY_4 is taken and it is assumed that N_j/N_0 for the levels $j > 20$ is insignificant, and (9*) determine the number of molecules on the level $j = 5$ at 300 K.

Vari- ant	XY_4	$r_{X-Y} \times 10^{10}, m$	Vari- ant	XY_4	$r_{X-Y} \times 10^{10}, m$
1	$^{12}C^1H_4$	1.093	14	$^{28}Si^{19}F_4$	1.540
2	$^{12}C^2H_4$	1.093	15	$^{29}Si^{19}F_4$	1.540
3	$^{12}C^3H_4$	1.093	16	$^{30}Si^{19}F_4$	1.540
4	$^{28}Si^1H_4$	1.480	17	$^{72}Ge^{19}F_4$	1.670
5	$^{28}Si^2H_4$	1.480	18	$^{119}Sn^{19}F_4$	1.840
6	$^{28}Si^3H_4$	1.480	19	$^{48}Ti^{19}F_4$	1.740
7	$^{72}Ge^1H_4$	1.527	20	$^{91}Zr^{19}F_4$	1.850
8	$^{72}Ge^2H_4$	1.527	21	$^{178}Hf^{19}F_4$	1.890
9	$^{72}Ge^3H_4$	1.527	22	$^{207}Pb^{19}F_4$	2.020
10	$^{119}Sn^1H_4$	1.701	23	$^{29}Si^1H_4$	1.480
11	$^{119}Sn^2H_4$	1.701	24	$^{29}Si^2H_4$	1.480
12	$^{119}Sn^3H_4$	1.701	25	$^{29}Si^3H_4$	1.480
13	$^{12}C^{19}F_4$	1.322			

CHAPTER 5

Vibration of Atoms in Molecules.
Vibration and Vibration-Rotation Spectra

Basic Equations and Symbols

The vibrations of diatomic molecules at low amplitudes are given approximately by the equation

$$f = -k_e (r - r_e) \tag{5.1}$$

where f is the force of interaction between atomic nuclei, N; k_e is the force constant, N/m; and r and r_e stand for the internuclear dis-

tance, m. For a harmonic oscillator, solution of Eq. (1.3) gives

$$\epsilon_{\text{vibr}} = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k_e}{\mu}} \quad (5.2)$$

where ϵ_{vibr} is the vibrational energy of atoms, v is the vibrational quantum number, and μ is the reduced mass. The quantity $\frac{1}{2\pi} \sqrt{\frac{k_e}{\mu}}$ equals ν_e which is the vibration frequency, s^{-1} . Substitution of ν_e by $c\omega_e$ yields

$$\epsilon_{\text{vibr}} = \left(v + \frac{1}{2}\right) hc\omega_e \quad (5.3)$$

where ω_e is the wave number, m^{-1} . Equation (5.1) is not adequate for high-amplitude vibrations. The potential energy is more or less adequately described by the Morse equation

$$U_r = D_e \{1 - e^{-\alpha(r-r_e)}\}^2 \quad (5.4)$$

in which U_r is the potential energy, and D_e and α are constants:

$$D_e = hc\omega_e/4x_e \quad (5.5)$$

$$\alpha = \sqrt{8\pi^2\mu\omega_e cx_e/h} \quad (5.6)$$

x_e being the anharmonicity constant.

For an anharmonic oscillator, the vibrational energy is given by the equation

$$\epsilon_{\text{vibr}} = \left(v + \frac{1}{2}\right) hc\omega_e - \left(v + \frac{1}{2}\right)^2 hc\omega_e x_e \quad (5.7)$$

In the vibrational spectra absorption of quanta is observed:

$$hc\tilde{\nu} = \epsilon_{\text{vibr}, v} - \epsilon_{\text{vibr}, 0} \quad (5.8)$$

where $\tilde{\nu}$ is the wave number of the absorption line maximum, $\epsilon_{\text{vibr}, v}$ is the vibrational energy at the v th vibrational quantum level, and $\epsilon_{\text{vibr}, 0}$ is the vibrational energy at the zeroth vibrational quantum level. The following bands are observed in the spectrum:

$$\tilde{\nu}_1 = \omega_e - 2\omega_e x_e \quad (5.9)$$

$$\tilde{\nu}_2 = 2\omega_e - 6\omega_e x_e \quad (5.10)$$

$$\tilde{\nu}_3 = 3\omega_e - 12\omega_e x_e \quad (5.11)$$

where $\tilde{\nu}_1$, $\tilde{\nu}_2$ and $\tilde{\nu}_3$ are the wave numbers of the fundamental absorption band of the first and second overtones. The maximum value of the vibrational quantum number is

$$v_{\text{max}} = (1 - x_e)/2x_e \quad (5.12)$$

The maximum vibrational energy is

$$\varepsilon_{\text{vibr. max}} = hc\omega_e/4x_e = D_e \quad (5.13)$$

For a molecule to be transferred from the zeroth to the maximal vibrational quantum level v_{max} the energy

$$\varepsilon_{\text{vibr. max}} - \varepsilon_{\text{vibr. 0}} = \frac{hc\omega_e}{4x_e} (1 - x_e)^2 \quad (5.14)$$

is required.

If a substance is in the gaseous state, molecular vibration is accompanied by rotation. The rotation-vibration energy is

$$\begin{aligned} \varepsilon_{\text{r-v}} &= \varepsilon_{\text{rot}} + \varepsilon_{\text{vibr}} \\ &= B_v j(j+1) + \varepsilon_{\text{vibr}} \end{aligned} \quad (5.15)$$

When a molecule passes from the zeroth to the first vibrational quantum level, the rotational state of the molecule changes. Then, the change in energy will be

$$\begin{aligned} \Delta\varepsilon_{\text{r-v}} &= \omega_e (1 - 2x_e) \\ &+ B_v [j'(j' + 1) - j''(j'' + 1)] \end{aligned} \quad (5.16)$$

If $\Delta j = +1$, an *R*-branch appears in the spectrum:

$$\tilde{\nu} = \omega_e (1 - 2x_e) + \frac{2B_v}{hc} (j+1) \quad (5.17)$$

And if $\Delta j = -1$, it is a *P*-branch that appears:

$$\tilde{\nu} = \omega_e (1 - 2x_e) - \frac{2B_v}{hc} j \quad (5.18)$$

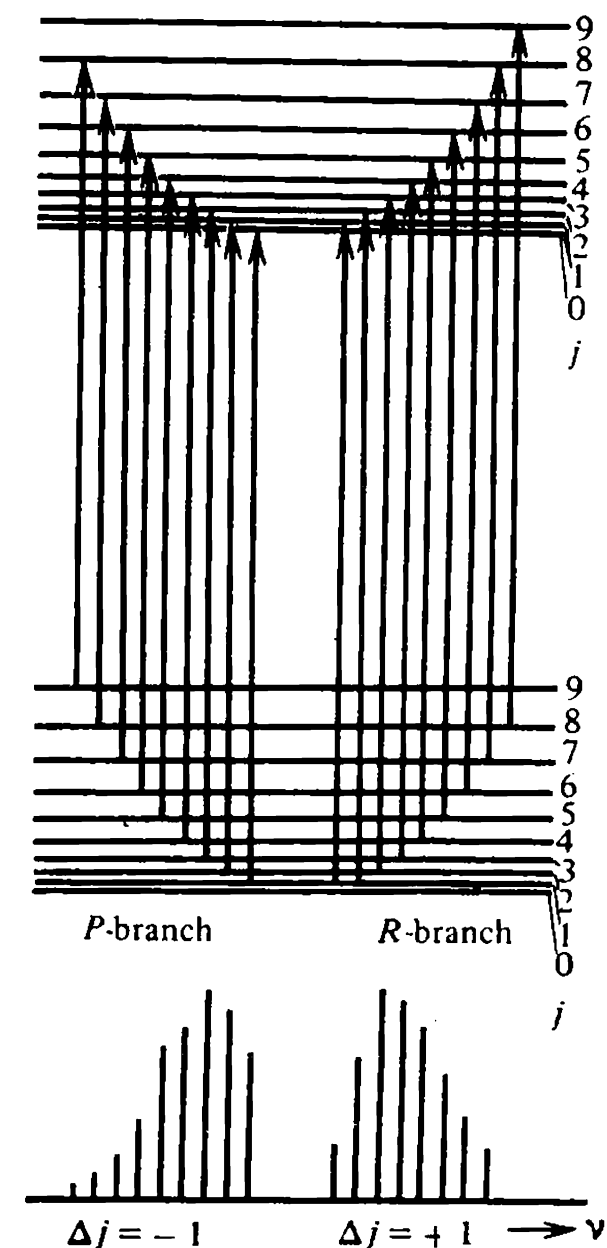


Fig. 8. Rotation-vibration energy levels, transition of molecules during light absorption, and rotation-vibration spectrum of diatomic molecules

Shown in Fig. 8 are the energy levels, transitions of molecules during absorption of electromagnetic radiation quanta, and the type of absorption spectrum for diatomic molecules. Equations (5.17) and (5.18) have been derived assuming that the rotational constant B_v depends on the vibrational energy. The rotational constant B_v varies inversely with the vibrational energy, which can be seen from

the equation

$$B_v = B_e - \alpha \left(v + \frac{1}{2} \right) \quad (5.19)$$

If Eq. (5.19) is taken into account, for the *R*-branch we shall have

$$\tilde{\nu} = \omega_e - 2\omega_e x_e + \frac{2B_e}{hc} (j+1) - \frac{1.5}{hc} \alpha (j+1)(j+2) \quad (5.20)$$

and for the *P*-branch,

$$\tilde{\nu} = \omega_e - 2\omega_e x_e - \frac{2B_e}{hc} j - \frac{1.5}{hc} \alpha (j-1)j \quad (5.21)$$

Exercises

1. The absorption spectrum of $^{19}\text{F}^{79}\text{Br}$ dissolved in a nonpolar solvent features the fundamental absorption band, which is more intense, and the first overtone, which is less intense. Their wave numbers are, respectively, 663.6×10^2 and $1318.2 \times 10^2 \text{ m}^{-1}$. Determine the frequency of vibration of the atoms in the molecule and the anharmonicity constant.

Solution. Substitute the values of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ into Eqs. (5.9) and (5.10) and solve these equations together:

$$663.6 \times 10^2 = \omega_e - 2\omega_e x_e \quad 3\omega_e - 6\omega_e x_e = 1990.8 \times 10^2$$

$$1318.2 \times 10^2 = 2\omega_e - 6\omega_e x_e \quad \frac{2\omega_e - 6\omega_e x_e}{\omega_e} = \frac{1318.2 \times 10^2}{672.6 \times 10^2 \text{ m}^{-1}}$$

$$2\omega_e x_e = 672.6 \times 10^2 - 663.6 \times 10^2 = 9.0 \times 10^2, \quad \omega_e x_e = 4.50 \times 10^2 \text{ m}^{-1}$$

$$x_e = 4.50 \times 10^2 / (672.6 \times 10^2) = 6.69 \times 10^{-3}$$

2. Find the maximal vibrational quantum number for $^{19}\text{F}^{79}\text{Br}$ if $\omega_e = 672.6 \times 10^2 \text{ m}^{-1}$ and $x_e = 6.69 \times 10^{-3}$.

Solution. Determine ν_{\max} using Eq. (5.12):

$$\nu_{\max} = (1 - 6.69 \times 10^{-3}) / (2 \times 6.69 \times 10^{-3}) = 74.23$$

Since the vibrational quantum number may only be an integer, the result must be rounded off: $\nu_{\max} = 74$. The value 74.23 is the result of differentiation in deriving Eq. (5.12), while function (5.7) is not a continuous one.

3. Determine the vibrational energy of atoms in the molecule $^{19}\text{F}^{79}\text{Br}$ on the zeroth and maximal vibrational quantum levels. Find the bond energy if $\omega_e = 672.6 \times 10^2 \text{ m}^{-1}$, $x_e = 6.69 \times 10^{-3}$, and $\nu_{\max} = 74$.

Solution. Calculate the vibrational energy using Eq. (5.7) in which zero is substituted for v :

$$\begin{aligned}\epsilon_{\text{vibr}} &= 0.5 \times 6.62 \times 10^{-34} \times 3 \times 10^8 \times 672.6 \times 10^2 \\ &\quad - 0.25 \times 6.62 \times 10^{-34} \times 3 \times 10^8 \times 672.6 \times 10^2 \\ &= 0.66 \times 10^{-20} \text{ J}\end{aligned}$$

The vibrational energy on the maximal vibrational quantum level is determined from Eq. (5.13):

$$\begin{aligned}\epsilon_{\text{max}} &= 6.62 \times 10^{-34} \times 3 \times 10^8 \times 672.6 \times 10^2 / (4 \times 6.69 \times 10^{-3}) \\ &= 49.89 \times 10^{-20} \text{ J}\end{aligned}$$

The bond energy is the difference between the vibrational energies on the maximal and zeroth vibrational levels times the Avogadro constant:

$$\begin{aligned}E_b &= (49.89 \times 10^{-20} - 0.66 \times 10^{-20}) 6.02 \times 10^{23} \\ &= 296.36 \times 10^3 \text{ J/mole}\end{aligned}$$

4. Determine the vibrational energies of atoms in the molecule $^{19}\text{F}^{79}\text{Br}$ on the vibrational quantum levels $v = 0, 1, 2, 3, 5, 8, 12, 20, 30$, and 74 if $\omega_e = 672.6 \times 10^2 \text{ m}^{-1}$, $x_e = 6.69 \times 10^{-3}$, and $v_{\text{max}} = 74$, and estimate the contribution of the second term in Eq. (5.7), which represents the departure of the vibration from the harmonic oscillator.

Solution. Given ω_e and $\omega_e x_e$, calculate the values of $hc\omega_e$ and $hc\omega_e x_e$, which are $133.58 \times 10^{-22} \text{ J}$ and $0.89 \times 10^{-22} \text{ J}$, respectively. Tabulate the results, writing separately the first and second terms of Eq. (5.7):

v	$(v + \frac{1}{2}) hc\omega_e \times 10^{22}, \text{ J}$	$(v + \frac{1}{2})^2 hc\omega_e x_e \times 10^{22}, \text{ J}$	$e \times 10^{22}, \text{ J}$
0	66.78	0.22	66.56
1	200.34	2.00	198.34
2	333.90	5.56	328.34
3	467.45	10.90	456.55
5	734.57	26.92	707.65
8	1135.24	64.30	1070.94
12	1669.48	139.11	1530.37
20	2737.94	374.07	2363.87
30	4073.52	827.97	3245.55
74	9950.07	4939.50	5010.57

The contribution of anharmonicity increases with the vibrational quantum number. On the zeroth and first vibrational quantum levels the vibrations are virtually harmonic.

5. Define the minimal and maximal distances between the atoms ^{19}F and ^{79}Br on the vibrational quantum levels $v = 0, 1, 2, 3, 5, 8, 12, 20, 30$, and 74. Plot $\varepsilon_{\text{vibr}} = f(r)$.

Solution. Solve Eqs. (5.4) and (5.7) together:

$$\left(v + \frac{1}{2}\right) hc\omega_e - \left(v + \frac{1}{2}\right)^2 hc\omega_e x_e = D_e \{1 - e^{-\alpha(r-r_e)}\}^2$$

The vibrational energies on all vibrational quantum levels are given in Problem 4. Calculate the constants D_e and α using Eqs. (5.5) and (5.6):

$$D_e = 133.58 \times 10^{-22} / (4 \times 6.69 \times 10^{-3}) = 0.5 \times 10^{-18} \text{ J}$$

$$\alpha = \sqrt{\frac{8 \times 3.14^2 \times 25.4 \times 10^{-27} \times 672.6 \times 10^2 \times 3 \times 10^8 \times 6.69 \times 10^{-3}}{6.62 \times 10^{-34}}} = 2.017 \times 10^{10}$$

Transform Eq. (5.4) to $1 - e^y = \sqrt{\varepsilon_{\text{vibr}}/D_e}$, where $y = -\alpha(r - r_e)$. The values of each factor in the transformed equation are listed in the table on p. 49. Plot $\varepsilon_{\text{vibr}} = f(r)$ from the tabulated data (Fig. 9).

6. Calculate the number of absorption maxima in the purely rotational spectrum of HF, taking the necessary data from the handbook.

Solution. Calculate the wave number of the fundamental band of HF:

$$\begin{aligned} \tilde{\nu} &= \omega_e (1 - 2x_e) \\ &= 4139 (1 - 0.043) = 3965 \text{ cm}^{-1} \end{aligned}$$

Calculate the rotational quantum number of the maximum in the purely rotational spectrum with the wave number $\tilde{\nu} = 3965 \text{ cm}^{-1}$:

$$\begin{aligned} \tilde{\nu} &= 2B_e (j + 1); \\ 3965 &= 2 \times 20.95 (j + 1); \quad j = 93 \end{aligned}$$

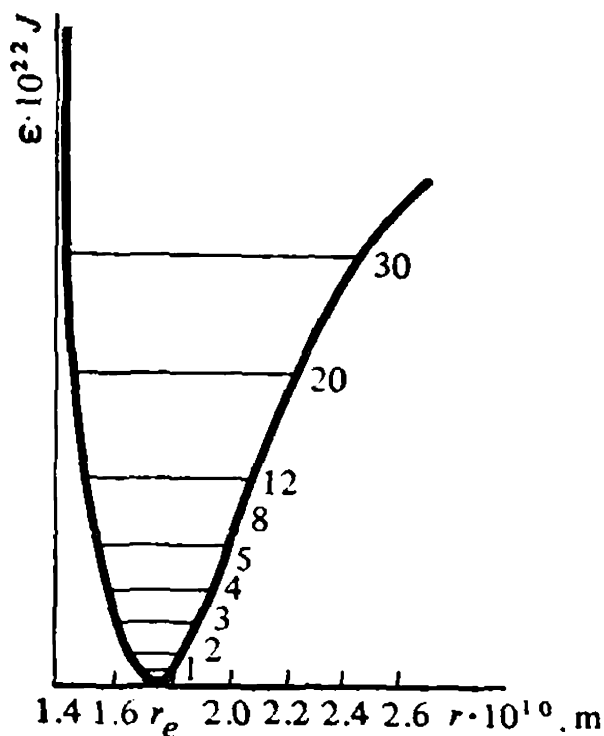


Fig. 9. Energy levels and vibration amplitudes of molecule $^{19}\text{F}^{79}\text{Br}$

7. Determine the wave numbers of absorption bands in the rotation-vibration absorption spectrum of $^{19}\text{F}^{79}\text{Br}$ if $\omega_e = 672.6 \times 10^2 \text{ m}^{-1}$ and $\omega_e x_e = 4.50 \times 10^2 \text{ m}^{-1}$. The rotational constant $B'_e = 0.714 \times 10^2 \text{ m}^{-1}$ and $\omega_e - 2\omega_e x_e = 663.6 \times 10^2 \text{ m}^{-1}$.

Solution. Determine the wave numbers of the absorption bands in the R-branch from Eq. (5.20). Calculate the wave numbers of the absorption bands in the P-branch using Eq. (5.21).

j	R-branch		P-branch	
	$B'_e(j+1) \times 10^{-2}, \text{m}^{-1}$	$\tilde{\nu} \times 10^{-2}, \text{m}^{-1}$	$B'_e j \times 10^{-2}, \text{m}^{-1}$	$\tilde{\nu} \times 10^{-2}, \text{m}^{-1}$
0	0.714	664.31	—	—
1	1.428	665.03	0.714	662.89
2	2.142	665.74	1.428	662.17
3	2.856	666.46	2.142	661.46
4	3.570	667.17	2.856	660.74
5	4.284	667.88	3.570	660.03
6	4.998	668.60	4.284	659.32
7	5.712	669.31	4.998	658.60
8	6.426	670.03	5.712	657.89
9	7.140	670.74	6.426	657.17
10	7.854	671.45	7.140	656.46

Problems

1. Determine the force constant k_e (N/m) for the molecule $^1\text{H}^{19}\text{F}$ if $\omega_e = 4.141 \times 10^5 \text{ m}^{-1}$.

2. Determine ω_e for $^2\text{H}^{19}\text{F}$ if for $^1\text{H}^{19}\text{F}$ $\omega_e = 4.141 \times 10^5 \text{ m}^{-1}$.

3. If the wave numbers of the absorption maxima in the fundamental band and the first overtone in the spectrum of the molecule $^{12}\text{C}^{16}\text{O}$ are $2.142 \times 10^5 \text{ m}^{-1}$ and $4.258 \times 10^5 \text{ m}^{-1}$, respectively, find the vibration frequency (m^{-1}) and the anharmonicity constant.

4. Given the values of the vibration frequency ω_e and the anharmonicity constant $\omega_e x_e$ (from the handbook) for the molecule CO, determine the vibrational energies on the zeroth and first vibrational quantum levels.

5. Determine the maximal vibrational quantum number, the vibrational energy on the zeroth and maximal vibrational quantum levels, and the bond energy per mole of $^1\text{H}^{19}\text{F}$.

6. Given the values of ω_e and $\omega_e x_e$ (from the handbook) for H_2 , determine the ratio of the number of molecules on the first vibrational quantum level to that of molecules on the zeroth level at 300 and 1000 K.

7. Given the values of ω_e and $\omega_e x_e$ (from the handbook) for I_2 , determine the relative population of molecules on the first vibrational quantum level at 300 and 1000 K.

8*. If $r_e = 0.7413 \times 10^{-10} \text{ m}$, $\omega_e = 3817.1 \times 10^2 \text{ m}^{-1}$, and $\omega_e x_e = 94.96 \times 10^2 \text{ m}^{-1}$ for the molecule $^1\text{H}^2\text{H}$, determine the vibrational energies on the 0th, 5th, 10th, 20th, and maximal vibrational quantum levels. Calculate $(r - r_e)$ using Eq. (5.4) and plot the Morse curve.

v	$E_{\text{vib}} \times 10^3, \text{J}$	$\frac{E_{\text{vib}}}{D} \times 10^4$	$\pm(1 - e^{\nu})$	e^{ν_1}	e^{ν_2}	$\log e^{\nu_1}$	$-\log e^{\nu_1}$	$-\nu_1$	$\log e^{\nu_2}$	ν_2	$(\nu_1 - \nu_2) \times 10^{10}$	$\nu_1 \times 10^{10}, \text{m}$	$-(\nu_2 - \nu_0) \times 10^{10}$	$\nu_2 \times 10^{10}, \text{m}$
0	66.56	133.12	0.1153	0.8847	1.1153	$\bar{1}.9468$	0.0532	0.1225	0.0474	0.1091	0.0607	1.8162	0.5409	1.7014
1	198.34	396.68	0.1992	0.8008	1.1992	$\bar{1}.9035$	0.0965	0.2222	0.0788	0.1814	0.1102	1.8657	0.0899	1.6656
2	328.34	656.68	0.2562	0.7438	1.2562	$\bar{1}.8715$	0.1285	0.2959	0.0990	0.2280	0.1467	1.9022	0.1131	1.6424
3	456.55	913.10	0.3022	0.6978	1.3022	$\bar{1}.8437$	0.1563	0.3599	0.1146	0.2639	0.1784	1.9339	0.1309	1.6246
5	707.65	1415.30	0.3762	0.6238	1.3762	$\bar{1}.7951$	0.2049	0.4718	0.1386	0.3191	0.2339	1.9894	0.1583	1.5972
8	1070.94	2141.88	0.4628	0.5372	1.4628	$\bar{1}.7302$	0.2698	0.6212	0.1652	0.3804	0.3080	2.0635	0.8870	1.5668
12	1530.37	3060.74	0.5533	0.4467	1.5533	$\bar{1}.6500$	0.3500	0.8059	0.1913	0.4405	0.3996	2.2551	0.2185	1.5370
20	2363.87	4727.74	0.6875	0.3125	1.6875	$\bar{1}.4949$	0.5051	1.1630	0.2272	0.5232	0.5766	2.3321	0.2595	1.4960
30	3245.55	6491.10	0.8057	0.1943	1.8057	$\bar{1}.2885$	0.7115	1.6383	0.2567	0.5911	0.8123	2.5678	0.2932	1.4623
74	5010.57	10021.14	1.0000	0.0000	2.0000				0.3010	0.6931			0.3436	1.4119

9. Calculate the wave numbers of the first three lines in the *P*-branch of the rotation-vibration absorption spectrum of $^1\text{H}^{19}\text{F}$, taking the necessary data from the handbook.

10. Determine the wave numbers of the first three lines in the *R*-branch of the rotation-vibration absorption spectrum of $^1\text{H}^{19}\text{F}$, taking the necessary data from the handbook.

11. In the *R*-branch of the rotation-vibration band of the absorption spectrum of gaseous $^1\text{H}^{35}\text{Cl}$, at 298 K and normal pressure, thirteen prominent maxima have emerged, their wave numbers and optical densities being tabulated below:

j	ω_e, cm^{-1}	D	j	ω_e, cm^{-1}	D	j	ω_e, cm^{-1}	D
0	2906.3	0.155	5	2997.8	0.362	9	3059.1	0.029
1	2925.8	0.418	6	3014.3	0.231	10	3072.8	0.011
2	2944.8	0.567	7	3030.9	0.129	11	3085.6	0.005
4	2980.9	0.497	8	3044.9	0.065	12	3098.4	0.001

Determine the number of molecules on each rotational quantum level if their extinction coefficient is independent of the rotational energy.

12*. Calculate the wave numbers of thirteen absorption bands in the *R*-branch of the rotation-vibration spectrum of $^1\text{H}^{35}\text{Cl}$, taking into account that the rotational constant B_v varies, $\omega_e = 2990.95 \text{ cm}^{-1}$, and $\omega_e x_e = 52.8185 \text{ cm}^{-1}$. Find the value of α in Eq. (5.19) from that of $\tilde{\nu}$ of the line $j = 12$ (see parameters of Problem 11). Compare the found wave numbers with the experimental ones, those given in Problem 11 or in the handbook.

13. The *P*-branch of the rotation-vibration spectrum of methane features lines with the following wave numbers (cm^{-1}): 3032.30, 3043.15, 3054.00, 3064.85, and 3075.70. Determine the moment of inertia of the methane molecule. The symmetry of this molecule is T_d . Find the equilibrium internuclear distance and compare it with the value given in the handbook.

14. Determine the number of the vibrational degrees of freedom of the linear molecule CS_2 (symmetry $D_{\infty h}$), the nonlinear molecule SO_2 (symmetry C_{2v}), the molecule NH_3 (symmetry C_{3v}), and the molecule CH_4 (symmetry T_d).

15. Three bands have been revealed in the IR absorption spectrum of MgF_2 at 240, 447, and 870 cm^{-1} . The latter band is the most intense, while the second band is the least intense. The symmetry of the molecule MgF_2 is C_{2v} . Identify the types of vibration associated with the above absorption bands.

16. Three bands have been revealed in the IR absorption spec-

trum of SnCl_4 , varying in intensity, at 104 (w), 129 (m), and 403 (s) cm^{-1} (w—weak, m—medium, s—strong). Identify the types of vibration associated with the above bands and determine the degeneracy of each vibration.

Multivariate Problems

1. Given the natural frequencies (ω_e) of vibration of atoms in molecule A and the anharmonicity constants ($\omega_e x_e$), (1) determine the wave number $\tilde{\nu}$ and the frequency ν of the absorption maxima corresponding to the transitions of molecules from the level $v = 0$ to the level $v = 1$ and from the level $v = 0$ to the level $v = 2$ at the same electronic state, (2) identify the spectral region (IR, visible or UV) accommodating the absorption bands corresponding to the above transitions, (3) determine the maximal value of the vibrational quantum number v_{\max} , (4) determine the vibrational energy on the zeroth and maximal vibrational quantum levels (J), (5) determine the bond energy in molecule A (J/mole), (6) determine the vibrational energy on two and three vibrational quantum levels in the range from $v = 0$ to v_{\max} , (7) plot the vibrational energy versus the vibrational quantum number, proceeding from the vibrational energies calculated above, and (8) determine the number of molecules on the zeroth and first vibrational quantum levels at 300 and 1000 K.

2. Proceeding from the parameters of Problem 1, determine for molecule A: (1) the wave numbers of the first three absorption lines in the *P*-branch of the rotation-vibration band and (2) the wave numbers of the first three lines in the *R*-branch of the rotation-vibration band.

Variant	Molecule A	ω_e, cm^{-1}	$\omega_e x_e, \text{cm}^{-1}$	Variant	Molecule A	ω_e, cm^{-1}	$\omega_e x_e, \text{cm}^{-1}$
1	$^1\text{H}^{35}\text{Cl}$	2990.95	52.82	14	$^2\text{H}^{81}\text{Br}$	1884.76	22.91
2	$^2\text{H}^{35}\text{Cl}$	2144.77	26.92	15	$^3\text{H}^{81}\text{Br}$	1548.14	15.45
3	$^3\text{H}^{35}\text{Cl}$	1775.86	18.36	16	$^{35}\text{Cl}^{19}\text{F}$	787.50	7.00
4	$^1\text{H}^{37}\text{Cl}$	2988.70	52.74	17	$^{37}\text{Cl}^{19}\text{F}$	777.99	6.83
5	$^2\text{H}^{37}\text{Cl}$	2140.95	26.82	18	$^{35}\text{Cl}^{79}\text{Br}$	443.10	1.80
6	$^3\text{H}^{37}\text{Cl}$	1770.35	18.25	19	$^{35}\text{Cl}^{81}\text{Br}$	441.42	1.79
7	$^1\text{H}^{79}\text{Br}$	2649.40	45.25	20	$^{37}\text{Cl}^{79}\text{Br}$	434.72	1.77
8	$^2\text{H}^{79}\text{Br}$	1885.33	22.73	21	$^{37}\text{Cl}^{81}\text{Br}$	433.01	1.76
9	$^3\text{H}^{79}\text{Br}$	1550.17	15.37	22	$^1\text{H}^{127}\text{I}$	2308.09	38.98
10	$^1\text{H}^{19}\text{F}$	4141.03	90.44	23	$^2\text{H}^{127}\text{I}$	1640.14	20.16
11	$^2\text{H}^{19}\text{F}$	3001.01	47.97	24	$^3\text{H}^{127}\text{I}$	1345.50	13.57
12	$^3\text{H}^{19}\text{F}$	2507.87	31.98	25	$^{12}\text{C}^{14}\text{N}$	2028.62	13.11
13	$^1\text{H}^{81}\text{Br}$	2649.03	45.25				

CHAPTER 6

First Law of Thermodynamics

Basic Equations and Symbols

For the final change in the state of a system the first law of thermodynamics is given by the equation

$$Q = \Delta U + W \quad (6.1)$$

where Q is the heat applied to or abstracted from the system, ΔU is the change in internal energy, and W is work. The sign of work is positive when it involves expansion of the system. The change in internal energy is

$$\Delta U = U_2 - U_1 \quad (6.2)$$

where U_1 and U_2 stand for the internal energy of the system at the beginning and end of the process, respectively;

$$H = U + PV \quad (6.3)$$

where H is the system's enthalpy;

$$\Delta H = \Delta U + \Delta (PV) \quad (6.4)$$

For ideal gases

$$\Delta H = \Delta U + \Delta n (RT) \quad (6.5)$$

where Δn is the change in the number of moles of gaseous substances;

$$\Delta n = \sum (v_i)_f - \sum (v_i)_i \quad (6.6)$$

The work of an isobaric process ($P = \text{const}$) is

$$W = P (V_2 - V_1) \quad (6.7)$$

where V_1 and V_2 are the volumes of the system at the beginning and end of the process, respectively. For ideal gases

$$W = nR (T_2 - T_1) \quad (6.8)$$

where T_1 and T_2 stand for the gas temperature at the beginning and end of the process, respectively, and R is the universal gas constant.

If one mole of an ideal gas is heated at constant pressure by 1°C , the work of the process will be

$$W^\circ = R \quad (6.9)$$

The work of an isochoric process ($V = \text{const}$) will be

$$W = 0 \quad (6.10)$$

The work of an isothermal process ($T = \text{const}$) with ideal gas expansion will be

$$W = Q = nRT \ln (V_2/V_1) = nRT \ln (P_2/P_1) \quad (6.11)$$

where n is the number of moles of the gas, and P_1 and P_2 are the gas pressures at the beginning and end of the process.

The work of an adiabatic process ($Q = 0$) will be

$$W = -\Delta U \quad (6.12)$$

$$W = nC_V (T_2 - T_1) \quad (6.13)$$

$$W = (P_1V_1 - P_2V_2)/(\gamma - 1) \quad (6.14)$$

$$W = \frac{nRT_1}{\gamma - 1} \left(1 - \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \right) \quad (6.15)$$

where C_V is the isochoric heat capacity of the gas, $\gamma = C_P/C_V$, P_1 and P_2 are the initial and the final pressure, C_P is the isobaric heat capacity of the gas, T_1 and T_2 are the initial and the final temperature, and V_1 and V_2 are the initial and the final volume, respectively. The pressure and volume at the initial and final states of the system are related through the following adiabatic equation:

$$P_1V_1^\gamma = P_2V_2^\gamma \quad (6.16)$$

The heat of the chemical reaction in an isochoric process ($V = \text{const}$) is

$$Q_V = \Delta U = U_2 - U_1 \quad (6.17)$$

In an isobaric process ($P = \text{const}$),

$$Q_P = \Delta H = H_2 - H_1 \quad (6.18)$$

The first corollary of Hess' law is given by the equation

$$\Delta H_T^\circ = \sum_1^i (\nu_i \Delta H_{f,T}^\circ)_f - \sum_1^i (\nu_i \Delta H_{f,T}^\circ)_i \quad (6.19)$$

where ν_i is the stoichiometric coefficient of the reaction, $\sum_1^i (\nu_i \Delta H_{f,T}^\circ)_f$ and $\sum_1^i (\nu_i \Delta H_{f,T}^\circ)_i$ are the sums of standard heats of formation of the final and initial substances involved in the reaction, $\Delta H_{f,T}^\circ$ being the heat of formation of a substance from simple substances under standard conditions at temperature T . Standard conditions imply that the substance is pure at a pressure of 1 atm. The standard state of a substance is denoted by a superscript "°".

The second corollary of Hess' law is given by the equation

$$\Delta H_T^\circ = \sum_1^i (\nu_i \Delta H_{\text{comb},T}^\circ)_f - \sum_1^i (\nu_i \Delta H_{\text{comb},T}^\circ)_i \quad (6.20)$$

where $\sum_1^i (\nu_i \Delta H_{\text{comb}, T}^\circ)_i$ and $\sum_1^i (\nu_i \Delta H_{\text{comb}, T}^\circ)_f$ are the sums of standard heats of combustion of the initial and final substances.

The temperature dependence of the heat capacity of substances is given by the following equations:

for the true heat capacity

$$C_V = \frac{dU}{dT}, \quad C_P = \frac{dH}{dT} \quad (6.21)$$

for ideal gases

$$C_P = C_V + R \quad (6.22)$$

The equation for the mean heat capacity \bar{C}_V at temperatures ranging from T_2 to T_1 takes the form

$$\bar{C}_V = (U_2 - U_1)/(T_2 - T_1), \quad \bar{C}_P = (H_2 - H_1)/(T_2 - T_1) \quad (6.23)$$

The mean and true heat capacities are related as follows:

$$\bar{C}_V = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_V dT, \quad \bar{C}_P = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_P dT \quad (6.24)$$

The temperature dependence of the heat capacity is given by the following equations:

for inorganic substances

$$C_P^\circ = a + bT + c'T^2 \quad (6.25)$$

for organic substances

$$C_P^\circ = a + bT + cT^2 + dT^3 \quad (6.26)$$

where a , b , c , c' , and d are coefficients defined empirically or from molecular-statistical calculations. The values of these coefficients are normally given in handbooks.

The temperature dependence of the enthalpy of a substance is expressed as

$$H_T^\circ - H_0^\circ = \int_0^T C_P^\circ dT \quad (6.27)$$

$$H_T^\circ - H_{298}^\circ = \int_{298}^T C_P^\circ dT \quad (6.28)$$

where H_0° is the substance's enthalpy at absolute zero, and $H_T^\circ - H_{298}^\circ$ is the enthalpy increment resulting from heating the substance from 298 K to T . If phase changes occur in the temperature range of T

to 298 K, Eq. (6.28) will take the following form:

$$H_T^\circ - H_{298}^\circ = \int_{298}^{T_{\text{recr}}} C_P^\circ dT + \Delta H_{\text{recr}} + \int_{T_{\text{recr}}}^{T_m} C_P^{\circ\prime} dT + \Delta H_m \\ + \int_{T_m}^{T_b} C_P^{\circ\prime\prime} dT + \Delta H_{\text{evap}} + \int_{T_b}^T C_P^{\circ\prime\prime\prime} dT \quad (6.29)$$

where ΔH_{recr} , ΔH_m , and ΔH_{evap} are the heats of recrystallization, melting, and evaporation, and C_P° , $C_P^{\circ\prime}$, $C_P^{\circ\prime\prime}$, and $C_P^{\circ\prime\prime\prime}$ are the heat capacities of the substance in the low-temperature crystalline, high-temperature crystalline, liquid, and gaseous states, respectively. The total (conditional) enthalpy of a substance at temperature T is

$$J_T^\circ = \Delta H_{f,298}^\circ + (H_T^\circ - H_{298}^\circ) \quad (6.30)$$

where J_T° is the total enthalpy of the substance at temperature T and standard pressure for the phase state which is stable at T , and $\Delta H_{f,298}^\circ$ is the standard heat of formation of the substance at 298 K.

The temperature dependence of the heat of chemical reaction is given by the equation

$$\frac{d\Delta H^\circ}{dT} = \sum_1^i (v_i C_P^\circ)_f - \sum_1^i (v_i C_P^\circ)_i = \Delta C_P^\circ \quad (6.31)$$

where $\sum_1^i (v_i C_P^\circ)_f$ and $\sum_1^i (v_i C_P^\circ)_i$ are the sums of the heat capacities of the final and initial substances, and ΔC_P° is the change in heat capacity in the course of the chemical reaction

$$\Delta C_P^\circ = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3 + \Delta c'/T^2 \quad (6.32)$$

The integral form of Eq. (6.31) will be

$$\Delta H_{T_2}^\circ = \Delta H_{T_1}^\circ + \int_{T_1}^{T_2} \Delta C_P^\circ dT \quad (6.33)$$

When some substances participating in a chemical reaction undergo phase changes, Eq. (6.33) is transformed to

$$\Delta H_{T_2}^\circ = \Delta H_{T_1}^\circ + \int_{T_2}^{T_{\text{recr}}} (\Delta C_P^\circ)' dT + \Delta H_{\text{recr}} + \int_{T_{\text{recr}}}^{T_m} (\Delta C_P^\circ)'' dT \\ + \Delta H_m + \int_{T_m}^{T_b} (\Delta C_P^\circ)''' dT + \Delta H_{\text{evap}} + \int_{T_b}^{T_2} (\Delta C_P^\circ)'''' dT \quad (6.34)$$

In calculating the heats of chemical reactions at a given temperature, one can use tables with mean values of heat capacities at temperatures ranging from 298 to T :

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^T \Delta \bar{C}_P^\circ dT = \Delta H_{298}^\circ + \Delta \bar{C}_P^\circ (T - 298) \quad (6.35)$$

If one or several substances undergo phase changes within a given temperature range, the best way to calculate the heat is by using tables of total enthalpies or tables of functions of $(H^\circ - H_{298}^\circ)_T$:

$$\Delta H_T^\circ = \sum_1^i (\nu_i J_i^\circ)_T - \sum_1^i (\nu_i J_i^\circ)_1 = \Delta H_{298}^\circ + \Delta (H^\circ - H_{298}^\circ)_T \quad (6.36)$$

$$\Delta (H^\circ - H_{298}^\circ)_T = \sum_1^i \nu_i (H^\circ - H_{298}^\circ)_{T, i} - \sum_1^i \nu_i (H^\circ - H_{298}^\circ)_{T, 1} \quad (6.37)$$

With phase changes in the temperature range of 298 K to T it is convenient to use the values of $(H_T^\circ - H_{298}^\circ)$ listed in the appendix for temperatures ranging from 298 to 1000 K.

Exercises

1. Determine the work of isobaric reversible expansion of three moles of an ideal gas while it is heated from 298 to 400 K.

Solution. The work of isobaric expansion is determined using Eq. (6.8):

$$W = 3 \times 8.3143 (400 - 298) = 2.544 \times 10^3 \text{ J}$$

2. Determine the work of evaporation of three moles of methanol at the normal boiling point.

Solution. The normal boiling point is the temperature at which boiling occurs at a normal external pressure of 1.0133×10^5 Pa. It is found in the handbook: $T_{n.b.} = 337.9$ K. The work is determined using Eq. (6.7) because the evaporation proceeds at a constant pressure. The final volume can be determined approximately from the law of ideal gaseous state:

$$V_2 = nRT_{n.b.}/P$$

In the first approximation, the volume V_1 of the liquid can be ignored since at temperatures far from the critical the volume of a liquid is much smaller than that of vapour. Then

$$W = PnRT_{n.b.}/P = nRT_{n.b.} = 3 \times 8.3143 \times 337.9 = 8.428 \times 10^3 \text{ J}$$

For the solution to be more exact find the densities of the liquid and vapour phases at $T_{n.b.}$ in the handbook: $d_{liq} = 0.7510 \times 10^3 \text{ kg/m}^3$; $d_v = 0.001222 \times 10^3 \text{ kg/m}^3$. From the densities we find the volumes

of three moles of the substance in the liquid and gaseous states:

$$V_1 = \frac{nM}{d_{\text{liq}}} = \frac{3 \times 32 \times 10^{-3}}{0.7510 \times 10^3} = 0.128 \times 10^{-3} \text{ m}^3$$

$$V_2 = \frac{nM}{d_v} = \frac{3 \times 32 \times 10^{-3}}{1.222} = 78.560 \times 10^{-3} \text{ m}^3$$

Since density is expressed in kg/m^3 , the molecular weight will be $M \times 10^{-3}$. Then

$$W = 1.0133 \times 10^5 (78.560 - 0.128) \times 10^{-3} = 7.9475 \times 10^3 \text{ J}$$

3. Determine the work of isothermal reversible expansion of three moles of water vapour from 0.5×10^5 to 0.2×10^5 Pa at 330 K. Under such conditions water vapour obeys the law of ideal gaseous state.

Solution. Determine the work using Eq. (6.11):

$$\begin{aligned} W &= 3 \times 8.3143 \times 330 \ln [0.5 \times 10^5 / (0.2 \times 10^5)] \\ &= 7.542 \times 10^3 \text{ J} \end{aligned}$$

4. Determine the work of adiabatic reversible expansion of three moles of argon from 0.05 to 0.50 m^3 . The initial temperature of the gas is 298 K.

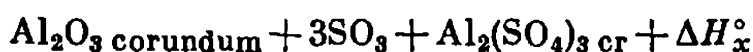
Solution. To determine the work of adiabatic expansion use Eq. (6.15). Determine the value of γ from C_P and C_V . Argon is a monatomic gas. Consequently, as follows from the molecular-kinetic theory of ideal gases, its isochoric heat capacity is $C_V = \frac{3}{2}R = 1.5 \times 8.3143 = 12.4715 \text{ J mole}^{-1} \text{ K}^{-1}$;

$$C_P = C_V + R = 12.4715 + 8.3143 = 20.7858 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\gamma = 20.7858 / 12.4715 = 1.667$$

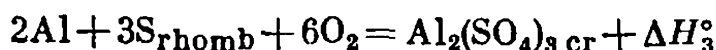
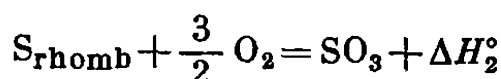
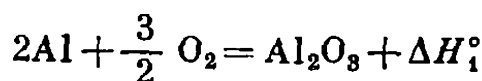
$$W = 3 \frac{8.3143 \times 298}{1.667 - 1} \left(1 - \frac{0.05^{0.667}}{0.50^{0.667}} \right) = 8.745 \times 10^3 \text{ J}$$

5. Determine the heat of the reaction



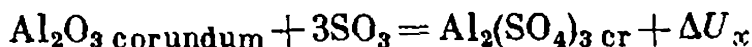
at 298 K and normal pressure.

Solution. To determine ΔH_x° use Eq. (6.19). The heats of formation of the initial and final substances in the standard state at 298 K are taken from the handbook:



$$\Delta H_x^\circ = \Delta H_3^\circ - \Delta H_1^\circ - 3\Delta H_2^\circ = -3434 + 1675 + 3 \times 395.2 = -573.4 \text{ kJ}$$

6. Determine the heat of the reaction



if the reaction proceeds at 298 K in an autoclave with a constant volume and the heat at $P = \text{const}$ is -573.4 kJ.

Solution. Determine the heat at a constant volume from that of the reaction using Eq. (6.5) (the change in the number of moles of the gaseous products of the reaction is $\Delta n = -3$ because Al_2O_3 and $\text{Al}_2(\text{SO}_4)_3$ are solids):

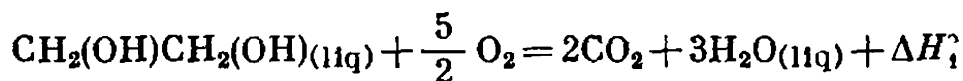
$$\begin{aligned}\Delta U_{298} &= \Delta H_{298}^\circ + 3 \times 8.3143 \times 298 = -573.4 \times 10^3 \\ &+ 7.433 \times 10^3 = -566.0 \times 10^3 \text{ J}\end{aligned}$$

7. Determine the heat of the reaction in which acetaldehyde is formed from glycol:

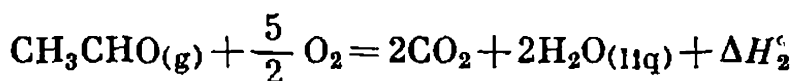


at 298 K and standard pressure.

Solution. Here it is more convenient to calculate the heat of the reaction from those of combustion. Find the heats of combustion of all the substances involved in the reaction in the handbook. Particular attention should be given to the combustion products and their phase states. Since in the reactions



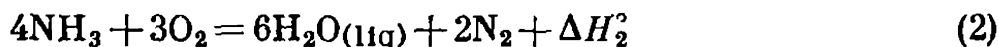
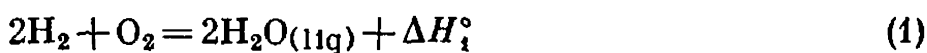
and



the heat of combustion of water is zero, $\Delta H_3^\circ = 0$. According to Eq. (6.20),

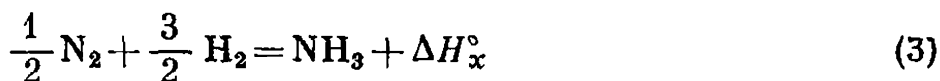
$$\Delta H_x^\circ = \Delta H_1^\circ - \Delta H_2^\circ - \Delta H_3^\circ = -1192.86 + 1192.44 = -0.42 \text{ kJ}$$

8. Calculate the heat of ammonia formation from simple substances at standard pressure and 298 K from the heats of the reactions



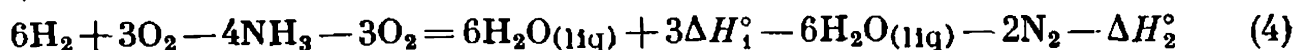
$$\Delta H_1^\circ = -571.68 \text{ kJ}, \quad \Delta H_2^\circ = -1530.28 \text{ kJ}$$

Solution. Write the equation of the reaction whose heat must be determined:



$\text{H}_2\text{O}_{(\text{liq})}$ and O_2 are not in Eq. (3), therefore, in order to exclude them from Eqs. (1) and (2), multiply Eq. (1) by three and subtract

Eq. (2) from it:



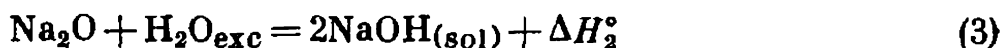
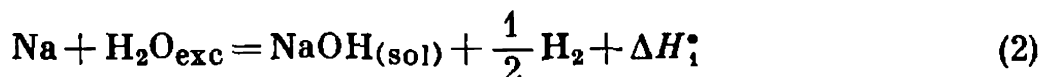
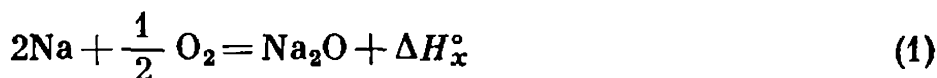
Transform Eq. (4) and divide it by 4:

$$\frac{3}{2} \text{H}_2 + \frac{1}{2} \text{N}_2 = \text{NH}_3 + (3\Delta H_1^\circ - \Delta H_2^\circ)/4$$

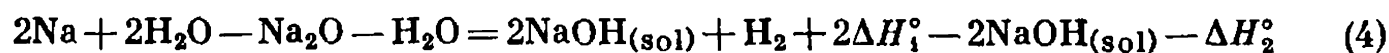
$$\begin{aligned} \Delta H_{f, 298}^\circ = \Delta H_x^\circ &= (3\Delta H_1^\circ - \Delta H_2^\circ)/4 \\ &= [3(-571.68) - (-1530.28)]/4 = -46.19 \text{ kJ/mole} \end{aligned}$$

9. The heats of solution of one mole of sodium and sodium oxide in water under standard conditions and at 298 K equal, respectively, -183.79 and -237.94 kJ/mole. In both cases, water is taken in highly excessive amounts. Calculate the heat $\Delta H_{f, 298}^\circ$ of sodium formation from simple substances under standard conditions and at 298 K.

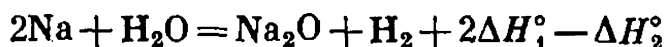
Solution. Write the equation of the reaction whose heat is to be determined, as well as those of the subordinate reactions:



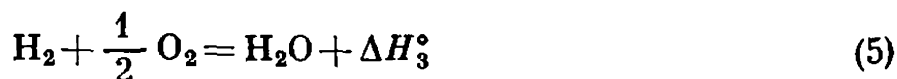
In order to exclude from Eqs. (2) and (3) $\text{NaOH}_{(\text{sol})}$ in excess of water, which does not participate in reaction (1), subtract Eq. (3) from Eq. (2) multiplied by two:



Transformation of Eq. (4) gives



In order to exclude H_2O and H_2 from Eq. (4) and to introduce O_2 , add Eq. (4) to the equation of the reaction in which simple substances yield water:



The value of ΔH_3° can be found in the handbook: -285.84 kJ/mole.

$$\begin{aligned} \Delta H_{f, 298}^\circ = \Delta H_x^\circ &= 2\Delta H_1^\circ - \Delta H_2^\circ + \Delta H_3^\circ = 2(-183.79) \\ &\quad - (-237.94) + (-285.84) = -415.48 \text{ kJ/mole} \end{aligned}$$

10. Determine the heat of dilution of a 30.8% aqueous solution of NaOH down to 0.442% at 298 K.

Solution. Find the integral heats of solution in the handbook. Since the concentrations listed there are expressed in moles H_2O

per mole NaOH, convert the concentrations:

$$\frac{30.8}{40.0} \text{ moles NaOH dissolved in } \frac{69.2}{18.0} \text{ moles H}_2\text{O}$$

$$1 \text{ mole NaOH dissolved in } x_1 \text{ moles H}_2\text{O}$$

$$x_1 = \frac{69.2 \times 40.0}{18.0 \times 30.8} = 5 \text{ moles H}_2\text{O per mole NaOH}$$

Similarly,

$$\frac{0.442}{40.0} \text{ mole NaOH dissolved in } \frac{99.557}{18.0} \text{ moles H}_2\text{O}$$

$$1 \text{ mole NaOH dissolved in } x_2 \text{ moles H}_2\text{O}$$

$$x_2 = \frac{99.558 \times 40.0}{18.0 \times 0.442} = 500 \text{ moles H}_2\text{O per mole NaOH}$$

The integral heats of solution of NaOH for the initial and final solution concentrations can be found in the handbook.

Number of moles H ₂ O per mole NaOH	5	500
ΔH_m° , kJ	-37.76	-42.36
$\Delta H_{\text{dil}}^\circ$	= -42.36 - (-37.76) = 4.6 kJ/mole	

Dilution of the NaOH solution is accompanied by release of heat.

11. Given the values of the isobaric heat capacities of methane at several temperatures:

T , K	300	400	500	600	700	800	900	1000
C_P° , J mole ⁻¹ K ⁻¹	35.80	40.74	46.56	52.50	58.07	63.27	67.27	72.06

solve an equation of the $C_P^\circ = f(T)$ type.

Solution. Since every experimental value of heat capacity contains a measurement error, to solve the equation

$$C_P^\circ = a + bT + cT^2$$

or, in other words, to find the coefficients a , b , and c , we shall resort to the least squares method:

$$\sum C_P^\circ = na + b \sum T + c \sum T^2$$

where n is the number of known heat capacity values (in this problem, $n = 8$):

$$\sum C_P^\circ T = a \sum T + b \sum T^2 + c \sum T^3$$

$$\sum C_P^\circ T^2 = a \sum T^2 + b \sum T^3 + c \sum T^4$$

To simplify the solution, let us introduce new variables:

$$x = (T - 300)/100, \quad y = C_P^\circ$$

T, K	y	x	x ²	x ³	x ⁴	xy	x ² y
300	35.80	0	0	0	0	0	0
400	40.74	1	1	1	1	40.74	40.74
500	46.56	2	4	8	16	93.12	186.24
600	52.50	3	9	27	81	157.50	472.50
700	58.07	4	16	64	256	232.28	929.12
800	63.27	5	25	125	625	316.35	1581.75
900	67.91	6	36	216	1296	407.46	2444.76
1000	72.06	7	49	343	2401	504.42	3530.94
Σ	436.91	28	140	784	4676	1751.87	9186.05

$$y = X + Yx + Zx^2$$

$$\frac{d \sum (y - X - Yx - Zx^2)^2}{dX} = -2 \sum (y - X - Yx - Zx^2) = 0$$

$$\frac{d \sum (y - X - Yx - Zx^2)^2}{dY} = -2 \sum (y - X - Yx - Zx^2) x = 0$$

$$\frac{d \sum (y - X - Yx - Zx^2)^2}{dZ} = -2 \sum (y - X - Yx - Zx^2) x^2 = 0$$

$$\sum (y - X - Yx - Zx^2) = 0$$

$$\sum (y - X - Yx - Zx^2) x = 0$$

$$\sum (y - X - Yx - Zx^2) x^2 = 0$$

$$\sum X = nX$$

$$\sum y = nX + Y \sum x + Z \sum x^2 \quad (a)$$

$$\sum xy = X \sum x + Y \sum x^2 + Z \sum x^3 \quad (b)$$

$$\sum x^2y = X \sum x^2 + Y \sum x^3 + Z \sum x^4 \quad (c)$$

Substitution of the values of $\sum x^2y$, $\sum x^2$, $\sum x^3$, and $\sum x^4$ into Eqs. (a) through (c) gives

$$436.91 = 8X + 28Y + 140Z \quad (a')$$

$$1751.87 = 28X + 140Y + 784Z \quad (b')$$

$$9186.05 = 140X + 784Y + 4676Z \quad (c')$$

By solving simultaneously Eqs. (a') through (c') we find X , Y , and Z :

$$\begin{array}{rcl}
 3058.37 & = & 56X + 196Y + 980Z \\
 3503.74 & = & 56X + 280Y + 1568Z \\
 \hline
 445.37 & = & 84Y + 588Z \\
 8759.35 & = & 140X + 700Y + 3920Z \\
 9186.05 & = & 140X + 784Y + 4676Z \\
 \hline
 426.80 & = & 84Y + 756Z \\
 445.37 & = & 84Y + 588Z \\
 426.80 & = & 84Y + 756Z \\
 \hline
 -18.67 & = & 168Z \quad Z = -0.111 \\
 Y & = & \frac{445.37 + 588 \times 0.111}{84} = 6.079 \\
 X & = & \frac{3058.37 - 196 \times 6.079 + 980 \times 0.111}{56} = 35.279
 \end{array}$$

$$\begin{aligned}
 C_P^\circ &= 35.279 + 6.079 \frac{T-300}{100} - 0.111 \left(\frac{T-300}{100} \right)^2 \\
 &= 35.279 + 6.079 \times 10^{-2}T - 18.237 - 0.111 \times 10^{-4}T^2 + 0.666 \times 10^{-2}T \\
 &\quad - 0.999 = 16.043 + 67.45 \times 10^{-3}T - 11.1 \times 10^{-6}T^2
 \end{aligned}$$

Thus,

$$C_P^\circ = 16.043 + 67.45 \times 10^{-3}T - 11.1 \times 10^{-6}T^2$$

12. Calculate the mean heat capacity \bar{C}_P of ammonia at temperatures ranging from 298 to 1000 K.

Solution. The mean heat capacity is calculated using Eq. (6.24). For the equation $C_P^\circ = f(T)$, see the handbook:

$$C_P^\circ = 29.80 + 25.48 \times 10^{-3}T - \frac{1.67 \times 10^5}{T^2}$$

This equation holds in the temperature range of 298 to 1800 K:

$$\begin{aligned}
 \bar{C}_P &= \frac{1}{1000-298} \int_{298}^{1000} \left(29.80 + 25.48 \times 10^{-3}T - \frac{1.67 \times 10^5}{T^2} \right) dT \\
 &= 0.001425 \left[29.80 (1000 - 298) + 12.74 \times 10^{-3} (1000^2 - 298^2) \right. \\
 &\quad \left. + 1.67 \times 10^5 \left(\frac{1}{1000} - \frac{1}{298} \right) \right] = 29.81 + 16.54 - 0.56 \\
 &= 45.79 \text{ J mole}^{-1} \text{ K}^{-1}
 \end{aligned}$$

13. Calculate the change in enthalpy when AgCl is heated from 298 to 1000 K at standard pressure ($H_{1000}^\circ - H_{298}^\circ$) and the total enthalpy of AgCl at 1000 K. At 728 K, AgCl melts. ΔH_m at the melting point is 13.21 kJ/mole. The temperature dependence of AgCl_(s) can be found in the handbook. The heat capacity of liquid AgCl at temperatures

ranging from 728 to 1000 K remains virtually constant and equal to $66.99 \text{ J mole}^{-1} \text{ K}^{-1}$.

Solution. Determine the heat of AgCl heating using Eq. (6.29), assuming a single phase change in the given temperature range:

$$H_T^\circ - H_{298}^\circ = \int_{298}^{728} C_{P(s)}^\circ dT + \Delta H_m + \int_{728}^{1000} C_{P(lq)}^\circ dT$$

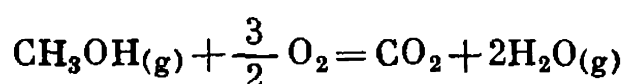
$$C_{P(s)}^\circ = 62.26 + 4.18 \times 10^{-3}T - \frac{11.30 \times 10^5}{T^2}$$

$$\begin{aligned} H_T^\circ - H_{298}^\circ &= \int_{298}^{728} \left(62.26 + 4.18 \times 10^{-3}T - \frac{11.30 \times 10^5}{T^2} \right) dT \\ &\quad + 13.21 \times 10^3 + \int_{728}^{1000} 66.99 dT = 62.26 (728 - 298) \\ &\quad + 2.09 \times 10^{-3} (728^2 - 298^2) + 11.30 \times 10^5 \left(\frac{1}{728} - \frac{1}{298} \right) \\ &\quad + 13.21 \times 10^3 + 66.99 (1000 - 728) = 56.88 \times 10^3 \text{ J/mole} \end{aligned}$$

Calculate the total enthalpy using Eq. (6.30), the value of $\Delta H_{f, 298}^\circ$ being found in the handbook:

$$J_{1000}^\circ = -126.8 + 56.88 = -69.92 \text{ kJ/mole}$$

14. Determine the heat of the reaction



at 500 K. The heat capacities of all the substances involved in the reaction are constant and equal to $C_{P, 298}^\circ$.

Solution. The heat of the reaction is determined using Eq. (6.33) where

$$\Delta C_P^\circ = \Delta C_{P, 298}^\circ = \text{const}$$

The necessary values of the heat of the reaction at 298 K and the change in heat capacity can be found from the heats of formation of all substances and heat capacities listed in the handbook:

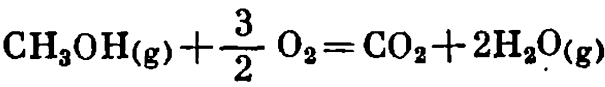
Substance	CO ₂	H ₂ O _(g)	O ₂	CH ₃ OH _(g)
$\Delta H_{f, 298}^\circ$, J/mole	-393.51	-241.84	0	-201.2
$C_{P, 298}^\circ$, J mole ⁻¹ K ⁻¹	37.13	33.56	29.36	43.9

$$\Delta H_{298}^\circ = (-393.51) + 2(-241.84) - (-201.2) = -675.99 \text{ kJ}$$

$$\Delta C_{P, 298}^\circ = 37.13 + 2 \times 33.56 - 43.9 - \frac{3}{2} 29.36 = 16.31 \text{ J/K}$$

$$\Delta H_{500}^\circ = -675.99 \times 10^3 + 16.31 (500 - 298) = -672.7 \times 10^3 \text{ J}$$

15. Determine the heat of the reaction



at 500 K and standard pressure. The calculation should be based on the mean heat capacities of the substances in the temperature range of 298 to 500 K.

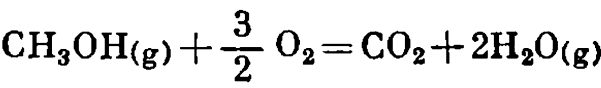
Solution. To determine ΔH°_{500} use Eq. (6.35). The heat of the reaction at 298 K is -675.99 kJ. The values of mean heat capacities \bar{C}_P for the above temperature range can be found in the handbook:

Substance	CO ₂	H ₂ O _(g)	O ₂	CH ₃ OH _(g)
\bar{C}_P , J mole ⁻¹ K ⁻¹	42.05	34.48	30.29	52.21

Hence, $\Delta \bar{C}_P = 13.365$ J mole⁻¹ K⁻¹,

$$\Delta H^\circ_{500} = -675.99 \times 10^3 + 13.365 (500 - 298) = -673.29 \times 10^3 \text{ J}$$

16. Write the equation for the temperature dependence of the heat of the reaction



at temperatures ranging from 1000 to 298 K.

Solution. To derive the equation $\Delta H_T^\circ = f(T)$ use Eq. (6.33). First, determine the temperature dependence of the change in heat capacity, which is given by Eq. (6.32). The coefficients a , b , c , and c' in Eqs. (6.25) and (6.26) can be found in the handbook:

Substance	$C_P^\circ = f(T)$, J mole ⁻¹ K ⁻¹				Temperature range, K
	a	$b \times 10^3$	$c' \times 10^{-5}$	$c \times 10^6$	
CO ₂	44.14	9.04	-8.54	0	298-2500
H ₂ O _(g)	30.00	10.71	0.33	0	273-2500
CH ₃ OH _(g)	15.28	105.20	0	-31.04	298-1000
O ₂	31.46	3.39	-3.77	0	273-2000
$\Sigma (\nu_i C_P^\circ)_f$	104.14	32.46	-7.88	0	298-2500
$\Sigma (\nu_i C_P^\circ)_l$	62.47	110.29	-5.66	-31.04	298-1000
ΔC_P°	43.67	-78.14	-2.22	31.04	298-1000

Hence, the equation of temperature dependence of the change in heat capacity for the above reaction at temperatures ranging from 298 to 1000 K will be

$$\Delta C_P^\circ = 43.67 - 78.14 \times 10^{-3}T + 31.04 \times 10^{-6}T^2 - 2.22 \times 10^5/T^2$$

Substitution of $\Delta C_P^\circ = f(T)$ under the sign of the integral and integration from 298 to T ($T \leq 1000$ K) give the following:

$$\Delta H_T^\circ = \Delta H_{298}^\circ$$

$$+ \int_{298}^T \left(43.67 - 78.14 \times 10^{-3}T + 31.04 \times 10^{-6}T^2 - \frac{2.22 \times 10^5}{T^2} \right) dT$$

$$\Delta H_T^\circ = -675.99 \times 10^3 + 43.67(T - 298) - 0.5 \times 78.14 \times 10^{-3}(T^2 - 298^2)$$

$$+ \frac{1}{3} 31.04 \times 10^{-6}(T^3 - 298^3) + 2.22 \times 10^5 \left(\frac{1}{T} - \frac{1}{298} \right)$$

$$= (675.99 - 9.44 + 3.46 - 0.27 - 0.74) 10^3$$

$$+ 43.67T - 38.91 \times 10^{-3}T^2 + 10.35 \times 10^{-6}T^3 + \frac{2.22 \times 10^5}{T}$$

$$= -682.98 \times 10^3 + 43.67T - 38.91 \times 10^{-3}T^2$$

$$+ 10.35 \times 10^{-6}T^3 + \frac{2.22 \times 10^5}{T}$$

Thus, we derive the desired equation for the given temperature range:

$$\Delta H_T^\circ = -682.98 \times 10^3 + 43.67T - 38.91 \times 10^{-3}T^2$$

$$+ 10.35 \times 10^{-6}T^3 + 2.22 \times 10^5/T^2$$

17. Determine the heat of the reaction $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ at 800 K and standard pressure.

Solution. Use the table of values of $(H_T^\circ - H_{298}^\circ)$ for the substances participating in the reaction. The heat of the reaction at any temperature can be determined from Hess' law:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \sum \nu_i (H_T^\circ - H_{298}^\circ)$$

where ΔH_{298}° is the heat of the reaction at 298 K, and $(H_T^\circ - H_{298}^\circ)$ is the change in enthalpy when the substance is heated from 298 K to T . The handbook contains the values of $\Delta H_{f, 298}^\circ$:

$$\Delta H_{298}^\circ = (-358.7 + 296.9 - 0) 10^3 = -61.8 \times 10^3 \text{ J}$$

and those of $(H_T^\circ - H_{298}^\circ)$ for the substances involved in the reaction:

T, K	$(H_T^\circ - H_{298}^\circ) \times 10^{-3}, \text{ J/mole}$			T, K	$(H_T^\circ - H_{298}^\circ) \times 10^{-3}, \text{ J/mole}$		
	SO ₂ Cl ₂	SO ₂	Cl ₂		SO ₂ Cl ₂	SO ₂	Cl ₂
298	0.000	0.000	0.000	700	35.087	18.590	14.424
300	0.167	0.084	0.064	800	44.466	23.740	18.134
400	8.248	4.271	3.538	900	53.970	29.058	21.860
500	16.874	8.793	7.109	1000	63.559	34.459	25.604
600	25.834	13.566	10.748				

$$\Delta H_{800}^\circ = (-61.8 \times 10^3 + 44.466 - 23.740 - 18.134) 10^3$$
$$= -59.208 \times 10^3 \text{ J}$$

18. Determine the heat of the reaction $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ at 700 K and standard pressure.

Solution. The choice of the approach to solve the problem of calculating the heat of a reaction involving condensed phases depends on whether the substances undergo a phase change within a given temperature range. To determine the phase state, find the phase change temperatures in the handbook:

Substance	Recrystallization ($\alpha \rightarrow \beta$) temperature, K	Melting point, K	Boiling point, K
α -NaOH	572	593	700
α -Na ₂ CO ₃	629	700	—

Both solids change their phase state at temperatures ranging from 298 to 700 K. As a result, use of Eq. (6.34) will complicate the calculation considerably. Therefore, it is preferable to use Eq. (6.36) in the calculation (see the appendix):

substance	α -NaOH	α -Na ₂ CO ₃	CO ₂	H ₂ O _(g)
$\Delta H_{f, 298}^\circ, \text{ kJ/mole}$	−426.6	−1129	−393.51	−241.84
$(H_{700}^\circ - H_{298}^\circ), \text{ kJ/mole}$	42.748	57.612	17.782	14.226

$$\Delta H_{298}^\circ = -1129 - 241.84 + 2 \times 426.6 + 393.51 = -124.13 \text{ kJ}$$
$$(H_{700}^\circ - H_{298}^\circ) = 57.612 + 14.226 - 2 \times 42.748 - 17.782$$
$$= -31.440 \text{ kJ}$$
$$\Delta H_{700}^\circ = -124.13 - 31.440 = -155.570 \text{ kJ}$$

Problems

1. Calculate the change in internal energy during evaporation of 20×10^{-3} kg of ethanol at the normal boiling point if its specific heat of evaporation is 837.38×10^3 J/kg and the specific volume of its vapour at the same temperature is 607×10^{-3} m³/kg. The volume of the liquid phase is to be ignored.

2. Determine the change in internal energy during evaporation of 1 kg of water at the normal boiling point if the heat of evaporation is 2258.7 J/kg. Assume that the water vapour is an ideal gas and ignore the volume of the liquid phase.

3. At 273 K and 1.0133×10^5 Pa, 5×10^{-3} m³ of krypton is heated to 873 K at a constant volume. Determine the final pressure of the gas and the heat expended in its heating.

4. A vessel having a volume of 5×10^{-2} m³ contains nitrogen at 200 K and 0.5×10^5 Pa. Determine the heat to be imparted to the gas for its pressure to go up to 2×10^5 Pa. Assume that nitrogen is an ideal gas under the above conditions. Find the parameters necessary for solution of this problem in the handbook.

5. At 298 K, 1×10^{-2} kg of oxygen is compressed adiabatically from 8×10^{-3} to 5×10^{-3} m³. Determine the final temperature, the work of compression, the change in internal energy, and the change in enthalpy if $C_V = \frac{5}{2}R$.

6. A vessel contains an unknown gas at 298 K. This gas is assumed to be nitrogen or argon. Sudden expansion of 5×10^{-3} m³ of this gas to 6×10^{-3} m³ has brought down its temperature by about 20 °C. Which of the two gases—argon or nitrogen—is in the vessel?

7. Determine the final temperature of the gases Ar, H₂, and H₂O if the pressure is increased or the volume is decreased ten-fold during adiabatic compression. The initial temperature is 298 K. Assume that the gases are ideal.

8. At 298 K, an ideal monatomic gas isothermally and reversibly expands from 1.5×10^3 to 10×10^3 m³ with 966×10^3 J of heat being absorbed in the process. Calculate the number of moles of the gas involved in the process.

9. A vessel contains 10^3 moles of an ideal monatomic gas at 273 K and 1.01×10^5 Pa. Calculate the final temperature of the gas, its pressure, and the work of its expansion to twice the initial volume in the case of: (a) slow isothermal expansion in a cylinder with a piston moving without friction; (b) adiabatic expansion under similar conditions; and (c) instantaneous removal of the partition separating the vessel from an evacuated space of the same volume. Explain the difference in the results obtained in the three cases.

10. Calculate the heat necessary for the temperature of 3×10^3 moles of ammonia to go from 273 up to 473 K at a constant pressure. Find the necessary parameters in the handbook.

11. Calculate the change in enthalpy during heating of 2 kg of α -SiO₂ from 298 to 800 K if the temperature dependence of heat capacity is given by the equation

$$C_P^\circ = 46.94 + 34.31 \times 10^{-3}T - 11.3 \times 10^5/T^2$$

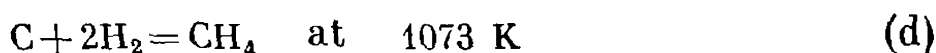
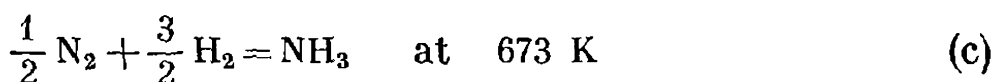
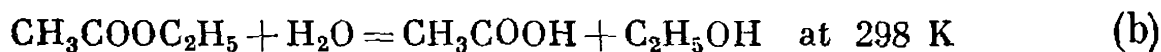
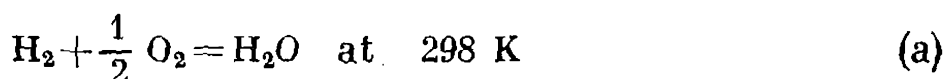
12. Determine the change in enthalpy during heating of 10 kg of gaseous methanol from 400 to 700 K at a pressure of 1.0133×10^5 Pa. Find the temperature dependence of heat capacity in the handbook.

13*. Given the temperature dependence of the heat capacity of solid heptane, find the change in enthalpy ($H_{182.5}^\circ - H_0^\circ$) for solid heptane by way of graphical integration. Determine the change in enthalpy in the process $C_7H_{16(s), 0 \text{ K}} \rightarrow C_7H_{16(lq), 182.5 \text{ K}}$ if the heat of melting of heptane at 182.5 K is 14.051×10^3 J/mole.

$T, \text{ K}$	$C_P^\circ, \text{ J mole}^{-1} \text{ K}^{-1}$	$T, \text{ K}$	$C_P^\circ, \text{ J mole}^{-1} \text{ K}^{-1}$	$T, \text{ K}$	$C_P^\circ, \text{ J mole}^{-1} \text{ K}^{-1}$
15.14	6.28	38.43	36.55	86.56	83.02
17.52	8.83	42.96	41.95	96.20	90.35
19.74	11.43	47.87	47.56	106.25	97.22
21.80	14.25	53.18	53.59	118.55	105.05
24.00	17.22	65.25	65.69	134.28	113.67
26.68	20.66	71.86	71.34	151.11	123.68
30.44	25.45	79.18	77.58	167.88	133.81
34.34	30.85				

14. Calculate the coefficient A in Debye's equation $C_V = AT^3$ for heptane if at 15.14 K $C_V = 6.28 \text{ J mole}^{-1} \text{ K}^{-1}$. Determine ($H_{15.14}^\circ - H_0^\circ$) using Debye's equation. Plot the change in enthalpy in the temperature range of 15.14 to 182.5 K, proceeding from the data of Problem 13. Calculate the change in enthalpy of solid heptane at temperatures ranging from 0 to 182.5 K.

15. Calculate the difference ($\Delta H^\circ - \Delta U$) at 1.0133×10^5 Pa in the following processes:



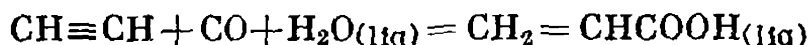
16. Determine the heat of the acrylic acid synthesis reaction $\text{CH}\equiv\text{CH} + \text{CO} + \text{H}_2\text{O}_{(lq)} = \text{CH}_2=\text{CHCOOH}_{(lq)}$ at standard

pressure and 298 K if the heats of formation (kJ/mole) are known:

Substance	$\text{CH}\equiv\text{CH}$	CO	$\text{H}_2\text{O}_{(\text{liq})}$	$\text{CH}_2=\text{CHCOOH}_{(\text{liq})}$
$\Delta H_f^\circ, 298, \text{ kJ/mole}$	226.75	-110.50	-285.84	-384.37

Also determine the heat of the same reaction at a constant volume.

17. Determine the heat of the reaction



at standard pressure and 298 K if the heats of combustion of the substances involved are known:

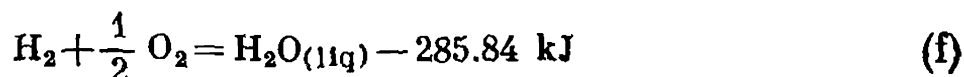
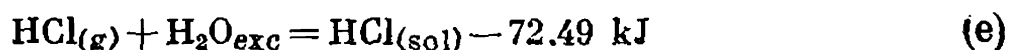
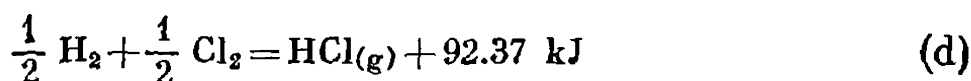
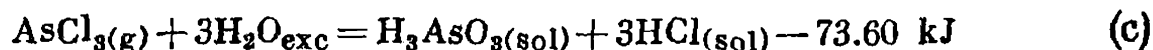
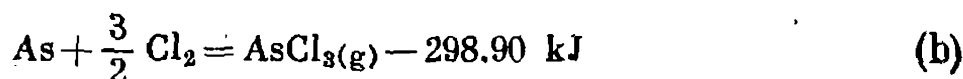
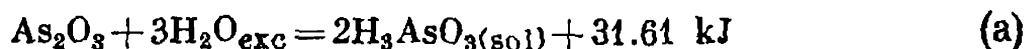
Substance	$\text{CH}\equiv\text{CH}$	CO	$\text{H}_2\text{O}_{(\text{liq})}$	$\text{CH}_2=\text{CHCOOH}_{(\text{liq})}$
$\Delta H_{\text{comb}}^\circ, 298, \text{ kJ/mole}$	-1299.63	-283.18	0	-1368.03

Also determine the heat of the same reaction at a constant volume.

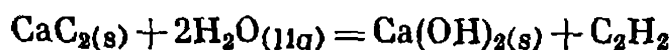
18. Calculate the heats of methane formation from simple substances at 298 K and standard pressure, as well as at $V = \text{const}$, proceeding from the following data: $\Delta H_f^\circ, 298 = -285.84 \text{ kJ/mole}$ for $\text{H}_2\text{O}_{(\text{liq})}$, $\Delta H_f^\circ, 298 = -393.51 \text{ kJ/mole}$ for CO_2 , and $\Delta H_{\text{comb}}^\circ, 298 = -890.31 \text{ kJ/mole}$ for CH_4 .

19. The heat of Fe_2O_3 formation from simple substances is -821.32 kJ/mole at 298 K and standard pressure, and that of Al_2O_3 formation is 1675.60 kJ/mole under the same conditions. Calculate the heat of the reaction of reduction of 1 mole Fe_2O_3 with metallic aluminium.

20. Determine the heat of As_2O_3 formation from simple substances at 298 K and standard pressure, proceeding from the following thermochemical equations:



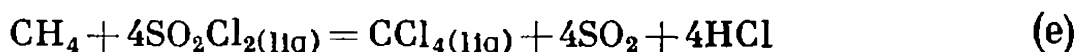
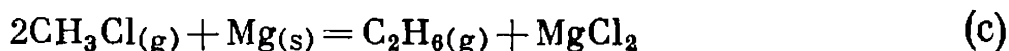
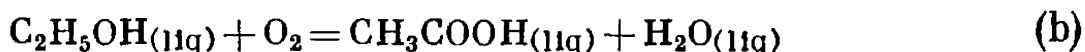
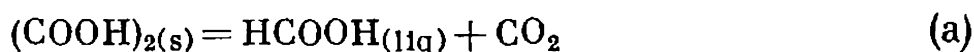
21. Calculate the heat of the reaction



at 298 K and standard pressure. Find the heats of formation necessary for the calculations in the handbook.

22. Determine the heat of formation of the following compounds from simple substances at standard pressure and 298 K: (a) liquid benzene C_6H_6 ; (b) liquid glycol $C_2H_6O_2$; (c) solid oxalic acid $(COOH)_2$; and (d) liquid aniline $C_6H_5NH_2$. Find the appropriate heats of combustion in the handbook.

23. Calculate the heats of the reactions



at 298 K and standard pressure.

24. When naphthalene burns in a calorimetric bomb at 298 K, yielding water and carbon dioxide, the heat of combustion is -5152.96 kJ/mole. Calculate the heat of combustion of naphthalene at a constant pressure if the water vapour resulting from the combustion (a) is condensed and (b) is not condensed.

25. A producer gas has the following composition (vol. %): CO 21.85, CO_2 7.12, H_2 13.65, CH_4 3.25, O_2 0.90, and N_2 53.23. Determine the heat of combustion of 1 m^3 of the producer gas at 1.0133×10^5 Pa and 298 K if the combustion is complete. The water vapour is not condensed.

26. Determine the heat of dilution of 100 kg of 77.76% nitric acid with water to 25.91%. For reference data, see the handbook.

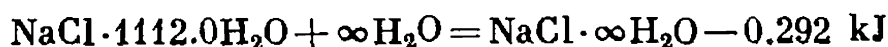
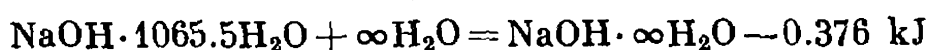
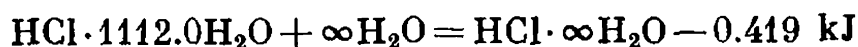
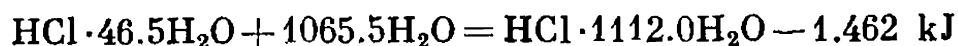
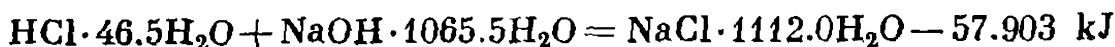
27. Determine the heat released when 0.1 kg of 50% sulphuric acid is added to 0.3 kg of water. Find the necessary heats of solution in the handbook.

28. Calculate the heat of mixing 0.5 kg of 20% sulphuric acid with 1 kg of 60% sulphuric acid. For reference data, see the handbook.

29. The heat of solution of anhydrous lithium sulphate is -26.71 kJ/mole. The heat of solution of crystal hydrate $LiSO_4 \cdot H_2O$ is 14.31 kJ/mole at 298 K. Calculate the heat of $LiSO_4 \cdot H_2O$ formation from the anhydrous salt and water. Determine the percentage content of water in partially weathered crystal hydrate of lithium sulphate if the heat of solution of 1 kg of this salt is -0.146×10^3 kJ.

30. Calculate the heat of neutralization of hydrochloric acid with sodium hydroxide in an infinitely dilute solution, proceeding from

the following data:



31. Determine the heat of formation of crystalline amino acetic acid $\text{NH}_2\text{CH}_2\text{COOH}$ at 298 K and standard pressure, knowing that the heat of its combustion is -976.72 kJ/mole . Compare the found value with that given in the handbook.

32. Determine the heat of combustion of crystalline *p*-nitrophenol, $\text{C}_6\text{H}_5\text{NO}_3$, at 298 K if the heat of its formation is $\Delta H_f^\circ, 298 = -191.66 \text{ kJ/mole}$. Compare the found value with that given in the handbook.

33. Determine the heat of the reaction $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2 (\text{liq})$ at 340 K, assuming that the heat capacities of all the reactants are independent of temperature and equal to those at 298 K. Find the heat capacity values in the handbook.

34. Determine the heat of the reaction $\text{Na}_{(\text{s})} + \frac{1}{2}\text{I}_{2(\text{s})} = \text{NaI}_{(\text{s})}$ at 370 K. The temperature dependence of heat capacities can be found in the handbook.

35. Write the equation of temperature dependence of the molar heat of combustion of hydrogen at a constant pressure; the resulting water vapour is not condensed. Define the temperature range within which the derived equation holds. Calculate the heat of the reaction at 800 K.

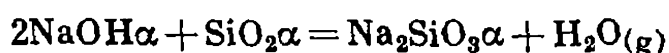
36. Derive the equation of temperature dependence of the heat of the reaction $\text{C}_{\text{gr}} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$. Calculate ΔH_{1000}° .

37. The heat of combustion of graphite at 298 K is -393.795 kJ/mole , while that of diamond's combustion at the same temperature is -395.692 kJ/mole . The specific heats for these substances are 720.83 and $505.58 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively. Calculate the heat of graphite's transformation into diamond at 273 K.

38. The heat of evaporation of methanol at 298 K is 37.5 kJ/mole . Determine the heat of methanol's evaporation at 320 K. Take the heat capacities of liquid and gaseous methanol from the handbook.

39. Calculate the heat of formation of AlCl_3 from simple substances at 423 K and standard pressure. Find the heat effect at 298 K and the temperature dependences of heat capacities in the handbook.

40*. Determine the heat of the reaction



at standard pressure and 800 K. Find the necessary parameters in the handbook. The heat of melting of NaOH at 595 K is 6.36 kJ/mole.

41*. Determine the heat of the reaction $S + O_2 = SO_2$ at 390 K and standard pressure. Take the necessary parameters from the handbook. At 390 K sulphur crystals are in the monoclinic form. The phase change temperature is 368.6 K.

42. Calculate the heat of the reaction $SO_2 + Cl_2 = SO_2Cl_2$ at 500 K. To do this, take the values of $(H_T^\circ - H_{298}^\circ)$ from p. 66.

43*. The heat capacities of *n*-propane at different temperatures are as follows:

T, K	300	400	500	600	700	800	900	1000
$C_P^\circ, J \text{ mole}^{-1} K^{-1}$	73.8	94.6	112.9	129.0	143.1	155.3	165.3	175.1

Express the analytical relation $C_P^\circ = f(T)$ as the power series $C_P^\circ = a + bT + cT^2$.

Multivariant Problems

1. Calculate the heat of reaction A at 298 K: (a) at $P = \text{const}$; (b) at $V = \text{const}$. The heats of formation of the substances involved in the reaction under standard conditions can be taken from the handbook.

Vari- ant	Reaction A	Vari- ant	Reaction A
1	$2H_2 + CO = CH_3OH_{(lq)}$	14	$SO_2 + Cl_2 = SO_2Cl_2$
2	$4HCl + O_2 = 2H_2O_{(lq)} + 2Cl_2$	15	$CO + 3H_2 = CH_4 + H_2O_{(lq)}$
3	$NH_4Cl_{(s)} = NH_3 + HCl$	16	$2CO + SO_2 = S_{\text{rhomb}} + 2CO_2$
4	$2N_2 + 6H_2O_{(lq)} = 4NH_3 + 3O_2$	17	$CO + Cl_2 = COCl_2(g)$
5	$4NO + 6H_2O_{(lq)} = 4NH_3 + 5O_2$	18	$CO_2 + H_2 = CO + H_2O_{(lq)}$
6	$2NO_2 = 2NO + O_2$	19	$CO_2 + 4H_2 = CH_4 + 2H_2O_{(lq)}$
7	$N_2O_4 = 2NO_2$	20	$2CO_2 = 2CO + O_2$
8	$Mg(OH)_2 = MgO + H_2O_{(g)}$	21	$CH_4 + CO_2 = 2CO + 2H_2$
9	$CaCO_3 = CaO + CO_2$	22	$C_2H_6 = C_2H_4 + H_2$
10	$Ca(OH)_2 = CaO + H_2O_{(g)}$	23	$C_2H_5OH_{(lq)} = C_2H_4 + H_2O_{(lq)}$
11	$S_{\text{rhomb}} + 2H_2O_{(lq)} = SO_2 + 2H_2$	24	$CH_3CHO_{(g)} + H_2 = C_2H_5OH_{(lq)}$
12	$S_{\text{rhomb}} + 2CO_2 = SO_2 + 2CO$	25	$C_6H_6_{(lq)} + 3H_2 = C_6H_{12}$
13	$2SO_2 + O_2 = 2SO_3$		

2. Calculate the heat of formation of substance A from simple substances at 298 K and standard pressure if its heat of combustion at the same temperature and pressure is known. The combustion proceeds to $CO_2(g)$ and $H_2O_{(lq)}$.

Variant	Substance A	Formula	State
1	Acetic acid	$C_2H_4O_2$	liq
2	1,1-Ethylene chloride	$C_2H_4Cl_2$	liq
3	Ethylene chloride	$C_2H_4Cl_2$	g
4	Ethylene glycol	$C_2H_6O_2$	liq
5	Dimethylamine	C_2H_7N	liq
6	Acetone	C_3H_6O	liq
7	Propylamine	C_3H_7N	liq
8	Isopropanol	C_3H_8O	liq
9	Propanol	C_3H_8O	liq
10	Glycerol	$C_3H_8O_3$	liq
11	Butyronitrile	C_4H_7N	liq
12	Butanol	$C_4H_{10}O$	liq
13	<i>tert</i> -Butanol	$C_4H_{10}O$	liq
14	Diethyl ether	$C_4H_{10}O$	liq
15	Pyridine	C_5H_5N	liq
16	Amyl alcohol	$C_5H_{12}O$	liq
17	Dichlorobenzene	$C_6H_4Cl_2$	liq
18	Nitrobenzene	$C_6H_5O_2N$	liq
19	Phenol	C_6H_6O	s
20	Hydroquinone	$C_6H_6O_2$	s
21	Aniline	C_6H_7N	liq
22	Cyclohexanol	$C_6H_{12}O$	liq
23	Benzoic acid	$C_7H_6O_2$	s
24	Benzyl alcohol	C_7H_8O	liq
25	Heptanol-1	$C_7H_{16}O$	liq

3. Calculate the heat released or absorbed during dilution of a kg of an aqueous $b\%$ solution of substance A in c kg of water at 298 K. (See the upper table on p. 74.) To do this, use the integral heats of solution given in the handbook.

4. Derive the analytical temperature dependence of the heat (J) of reaction A if the heat of this reaction at 298 K is known. The equations of the $C_P^\circ = f(T)$ type can be found in the handbook. Calculate the heat of the reaction at temperature T . Plot the relations

$$\sum_1^i (\nu_i C_P^\circ)_f = f(T); \quad \sum_1^i (\nu_i C_P^\circ)_1 = f(T); \quad \text{and} \quad \Delta H_T^\circ = f(T)$$

in the temperature range for which the equation $\Delta H_T^\circ = f(T)$ holds. Determine graphically $\frac{\partial \Delta H}{\partial T}$ at T_1 . Calculate C_P° at this temperature.

Variant	Substance A	a	b	c	Variant	Substance A	a	b	c
1	HCl	1	26	2	14	KOH	4	45	3
2	HCl	2	38	3	15	KOH	5	40	1
3	HCl	3	30	4	16	KOH	1	35	2
4	H ₂ SO ₄	4	90	1	17	HNO ₃	2	50	4
5	H ₂ SO ₄	5	80	2	18	HNO ₃	3	40	5
6	H ₂ SO ₄	1	70	3	19	NH ₃	4	30	10
7	H ₂ SO ₄	2	60	3	20	LiCl	5	30	3
8	HCl	3	34	1	21	LiBr	1	45	2
9	NaOH	4	30	1	22	NaBr	2	40	6
10	NaOH	5	25	2	23	KI	3	50	6
11	NaOH	1	40	3	24	NaCl	4	26	10
12	NaOH	2	35	4	25	NaI	5	30	10
13	KOH	3	50	2					

Variant	Reaction A	T, K	T ₁ , K
1	$2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}_{(g)}$	800	350
2	$4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O}_{(g)} + 2\text{Cl}_2$	750	650
3	$\beta\text{-NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$	455	450
4	$2\text{N}_2 + 6\text{H}_2\text{O}_{(g)} = 4\text{NH}_3 + 3\text{O}_2$	1300	1000
5	$4\text{NO} + 6\text{H}_2\text{O}_{(g)} = 4\text{NH}_3 + 5\text{O}_2$	1000	900
6	$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	700	500
7	$\text{N}_2\text{O}_4 = 2\text{NO}_2$	400	350
8	$\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}_{(g)}$	500	310
9	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$	1000	700
10	$\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}_{(g)}$	500	340
11	$\frac{1}{2} \text{S}_2 (g) + 2\text{H}_2\text{O}_{(g)} = \text{SO}_2 + 2\text{H}_2$	1000	900
12	$\frac{1}{2} \text{S}_2 (g) + 2\text{CO}_2 = \text{SO}_2 + 2\text{CO}$	900	850
13	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$	700	600
14	$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2 (g)$	400	300
15	$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}_{(g)}$	1000	900
16	$2\text{CO} + \text{SO}_2 = \frac{1}{2} \text{S}_2 (g) + 2\text{CO}_2$	900	700
17	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	400	350
18	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}_{(g)}$	1200	1000
19	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}_{(g)}$	1000	900
20	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$	700	500
21	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$	900	320
22	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$	400	350
23	$\text{C}_2\text{H}_5\text{OH}_{(g)} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}_{(g)}$	400	300
24	$\text{CH}_3\text{CHO}_{(g)} + \text{H}_2 = \text{C}_2\text{H}_5\text{OH}_{(g)}$	500	450
25	$\text{C}_6\text{H}_6 (g) + 3\text{H}_2 = \text{C}_6\text{H}_{12} (g)$	600	500

5. Determine the heat of reaction A at temperature T . Use the table of $(H_T^\circ - H_{298}^\circ)$ functions from the appendix.

Vari- ant	Reaction A	T , K	Vari- ant	Reaction A	T , K
1	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	500	14	$\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$	700
2	$\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$	500	15	$\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$	700
3	$\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$	500	16	$\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$	600
4	$\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$	400	17	$2\text{NaOH} + \text{CO}_2$ $= \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	700
5	$2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3$ $+ \text{H}_2\text{O}$	500	18	$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S}$	700
6	$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S}$	500	19	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	800
7	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	600	20	$\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$	800
8	$\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$	600	21	$\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$	700
9	$\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$	600	22	$2\text{NaOH} + \text{CO}_2$ $= \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	800
10	$\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$	500	23	$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S}$	800
11	$2\text{NaOH} + \text{CO}_2$ $= \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	600	24	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	900
12	$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S}$	600	25	$\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$	900
13	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	700			

CHAPTER 7

Second Law of Thermodynamics

Basic Equations and Symbols

The relationship between heat and work in a process based on Carnot's cycle is given by the equation

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{W}{Q_1} < 1 \quad (7.1)$$

in which η is the efficiency of the cycle, Q_1 is the amount of heat imparted, at temperature T_1 , to the system performing this cycle, Q_2 is the amount of heat given up by the system at T_2 , and W is the work performed by the system.

Among the basic properties of entropy is that in a reversible process, when the system passes from state 1 to state 2, the change in

entropy is

$$\Delta S = \int_1^2 \frac{\delta Q}{T} \quad (7.2)$$

where δQ is the elementary quantity of heat.

In an isolated system ($V, U = \text{const}$), entropy serves as a criterion of directness of a spontaneous process and the state of equilibrium:

$$\Delta S \geq 0 \quad (7.3)$$

The change in entropy during heating (cooling) from T_1 to T_2 at a constant volume or pressure is given by the equations

$$\Delta S = \int_{T_1}^{T_2} C_V \frac{dT}{T} \quad (7.4)$$

and

$$\Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T} \quad (7.5)$$

The change in entropy during heat absorption at a constant temperature and pressure or volume is calculated using the following formulas:

$$\Delta S = Q_P/T \quad (7.6)$$

$$\Delta S = Q_V/T \quad (7.7)$$

The change in entropy during isothermal expansion of n moles of an ideal gas can be determined from

$$\Delta S = nR \ln (V_2/V_1) \quad (7.8)$$

or

$$\Delta S = nR \ln (P_1/P_2) \quad (7.9)$$

The change in entropy during heat absorption by n moles of an ideal gas is given by the following equations:

$$\Delta S = nC_V \ln (T_2/T_1) + nR \ln (V_2/V_1) \quad \text{at } P = \text{const} \quad (7.10)$$

$$\Delta S = nC_P \ln (T_2/T_1) - nR \ln (P_2/P_1) \quad \text{at } V = \text{const} \quad (7.11)$$

The change in entropy during adiabatic expansion of an ideal gas is expressed as

$$\Delta S = nC_V \ln (P_2 V_2^\gamma / P_1 V_1^\gamma) \quad (7.12)$$

For a chemical reaction the change in entropy, ΔS_{reac} , is calculated using the equation

$$\Delta S_{\text{reac}} = \sum S_i^\circ - \sum S_j^\circ \quad (7.13)$$

where $\sum S_f^\circ$ and $\sum S_i^\circ$ are the sums of absolute entropies of the final and initial substances, respectively;

$$(\Delta S_{\text{reac}})_{T_2} = (\Delta S_{\text{reac}})_{T_1} + \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT \quad (7.13a)$$

The change in entropy for phase changes, $\Delta S_{\text{p.c.}}$, will be

$$\Delta S_{\text{p.c.}} = \Delta H_{\text{p.c.}}/T \quad (7.14)$$

Absolute entropy S_T° is calculated as follows:

$$S_T^\circ = \sum \int_0^T \frac{C_P^\circ dT}{T} + \sum \frac{\Delta H_{\text{p.c.}}}{T} - R \ln P_s \quad (7.15)$$

where the first sum expresses the change in entropy during heating, and the second sum, during phase changes; $R \ln P_s$ is the change in entropy during expansion (compression) of saturated vapour from equilibrium pressure to 1 atm.

The basic properties of the thermodynamic potentials include: Gibbs' energy G and Helmholtz' energy A :

$$P, T = \text{const}, \quad -\Delta G = W' \quad (7.16)$$

$$V, T = \text{const}, \quad -\Delta A = W' \quad (7.17)$$

where ΔG and ΔA are changes in Gibbs' and Helmholtz' energies, respectively, in any process, and W' is useful work. Gibbs' and Helmholtz' energies are criteria of directness of a spontaneous process and the state of equilibrium:

$$\text{at } P \text{ and } T = \text{const} \quad \Delta G \leq 0 \quad (7.18)$$

$$\text{at } V \text{ and } T = \text{const} \quad \Delta A \leq 0 \quad (7.19)$$

$$\Delta A = \Delta U - T\Delta S \quad (7.20)$$

$$\Delta G = \Delta H - T\Delta S \quad (7.21)$$

where ΔA , ΔU , ΔS , ΔG , and ΔH stand for the change in the corresponding functions in any physicochemical process; at $T = \text{const}$

$$\Delta G = \Delta A + \Delta(PV) \quad (7.22)$$

For ideal gases at $T = \text{const}$

$$\Delta G = \Delta A + \Delta nRT \quad (7.23)$$

where Δn is the change in the number of moles of the gaseous substances involved in a physicochemical process.

The changes in Gibbs' and Helmholtz' energies during heating (cooling) from T_1 to T_2 at a constant pressure or volume are expressed

by the following differential equations:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S' \quad (7.24)$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S' \quad (7.25)$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S' \quad (7.26)$$

$$\left(\frac{\partial \Delta A}{\partial T}\right)_{\Delta V} = -\Delta S' \quad (7.27)$$

and the following integral equations:

$$G_{T_2} - G_{T_1} = \int_{T_1}^{T_2} -S dT; \quad \Delta G_{T_2} - \Delta G_{T_1} = \int_{T_1}^{T_2} -\Delta S dt$$

$$A_{T_2} - A_{T_1} = \int_{T_1}^{T_2} -S dT; \quad \Delta A_{T_2} - \Delta A_{T_1} = \int_{T_1}^{T_2} -\Delta S dT$$

Within a narrow temperature range, if $C_P = \text{const}$, then

$$G_2 - G_1 = \Delta G = (C_P - S_{T_1})(T_2 - T_1) - C_P T_2 2.3 \log (T_2/T_1) \quad (7.28)$$

The changes in Gibbs' and Helmholtz' energies during compression or expansion at $T = \text{const}$ are given by the following differential equations:

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad (7.29)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (7.30)$$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \quad (7.31)$$

(where ΔV is the change in volume in the course of a physicochemical process) as well as by the following integral equations:

for ideal gases

$$A_2 - A_1 = \Delta A = RT \ln (V_1/V_2) \quad (7.32)$$

$$G_2 - G_1 = RT \ln (P_2/P_1) \quad (7.33)$$

for condensed systems at moderate pressures

$$G_2 - G_1 = V_{c.p.} (P_2 - P_1) \quad (7.34)$$

where $V_{c.p.}$ is the condensed phase volume; for chemical reactions ($T = \text{const}$)

$$\Delta G_{i, \text{reac}} = \sum_i (\Delta G_i)_f - \sum_i (\Delta G_i)_i \quad (7.35)$$

where $\sum_i (\Delta G_i)_f$ and $\sum_i (\Delta G_i)_i$ are the sums of Gibbs' energies for the final and initial substances;

$$\Delta G^\circ_{\text{reac}} = \sum_i (\Delta G^\circ_i)_f - \sum_i (\Delta G^\circ_i)_i \quad (7.36)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7.37)$$

where ΔG° , ΔH° , and ΔS° stand for the changes in the respective functions, occurring in a reaction in which a given compound is formed from simple substances at temperature T and under standard conditions.

The change in Gibbs' energy for phase changes is

$$\Delta G_{\text{p.c.}} = 0 \quad (7.38)$$

For evaporation and sublimation this change is

$$\Delta A_{\text{p.c.}} = RT \quad (7.39)$$

and for melting and polymorphous transformations it is

$$\Delta A_{\text{p.c.}} = 0 \quad (7.40)$$

Exercises

1. At the initial temperature of 373 K, one mole of oxygen goes through a cycle in an ideal Carnot engine. At first, it expands isothermally to twice the initial volume, then adiabatically to thrice the initial volume, after which oxygen is compressed isothermally to such a volume which will enable it to return to the original state as a result of the subsequent adiabatic compression. Assuming that $\gamma = C_P/C_V = 1.4$, calculate the work performed by the gas at each stage of the cycle, the work produced by the heat within the cycle, and the cycle efficiency.

Solution. 1. For the first stage of the cycle, which is the isothermal process, the work is determined from the equation

$$W_T = nRT (V_2/V_1) = Q_T$$

whence

$$W_1 = 8.314 \times 373 \times 2.3 \log (2V_2/V_1) = 2146.06 \text{ J}$$

2. For the second stage of the cycle, which is the adiabatic process, the work is determined from the equation

$$W_2 = nR \frac{T_1 - T_2}{\gamma - 1}$$

the temperature T_2 being determined as follows:

$$T_2 = T_1 \left(\frac{2V_1}{3V_1} \right)^{\gamma-1}; \quad T_2 = 373 \left(\frac{2}{3} \right)^{0.4} = 317.2 \text{ K}$$

Hence,

$$W_2 = 8.314 \frac{373 - 317.2}{0.4} = 1159.8 \text{ J}$$

3. For the third stage of the cycle, the work will be negative because the gas undergoes compression, $W_3 = -nRT \ln(V_3/V_4)$, where, as stated in the problem, $V_3 = 3V_1$ and the volume V_4 is to meet the condition that after the adiabatic compression the gas must return to the original state, consequently,

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_1}{T_2}$$

whence

$$V_4 = V_1 \sqrt[\gamma-1]{\frac{T_1}{T_2}}; \quad V_4 = V_1 \sqrt[0.4]{\frac{373}{317.2}} = 1.5V_1$$

Thus,

$$W_3 = -8.314 \times 317.2 \times 2.3 \log(3V_1/1.5V_1) = -1824.86 \text{ J}$$

4. For the fourth stage of the cycle, the work of the adiabatic process will be negative and numerically equal to that for the second stage because as a result of the adiabatic expansion the gas returns to the original state in terms of temperature:

$$\dot{W}_4 = -nR \frac{T_1 - T_2}{\gamma - 1} = 1159.8 \text{ J}$$

The total work throughout the cycle, $W = W_1 + W_2 + W_3 + W_4$, will be

$$W = 2146.06 - 1824.86 = 321.2 \text{ J}$$

The cycle efficiency $\eta = W/Q_1$, where $Q_1 = A_1$;

$$\eta = \frac{321.2}{2146.06} = 14.96\%$$

We shall have the same result if η is determined using Eq. (7.1):

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{373 - 317.2}{373} = 14.96\%$$

2. Two communicating vessels divided by a partition contain one mole of nitrogen and two moles of oxygen. The partition is removed, and the gases mix. Calculate the change in entropy, ΔS_{mix} , if the initial temperatures and pressures are the same, while the volumes are different: $V_{\text{N}_2} = 1$ litre; $V_{\text{O}_2} = 2$ litres. The final pressure of the mixture equals the initial pressure of the gases.

Solution. The gas mixing process is irreversible, and the change in entropy is given by the inequality

$$\Delta S > \int_1^2 \frac{\delta Q}{T}$$

But if the irreversible and reversible processes are conducted under the same boundary conditions, then $\Delta S_{rev} = \Delta S_{irrev}$. Any irreversible process can be mentally conducted in a reversible manner in several steps under the same boundary conditions, and the entropy for each reversible step can be calculated. Then, the sum of changes in entropy for these steps will equal the change in entropy for the irreversible process. In this problem, the total change in entropy can be substituted by the sum of changes in entropy due to separate expansion of each gas; that is, it can be assumed that $\Delta S_{mix} = \Delta S_{N_2} + \Delta S_{O_2}$. According to Eq. (7.3):

$$\Delta S_{N_2} = R \ln (V/V_{N_2}); \quad \Delta S_{O_2} = R \ln (V/V_{O_2})$$

$$V = V_{N_2} + V_{O_2} = 1 + 2 = 3$$

and

$$\Delta S_{mix} = -2.3 \times 8.31 (\log 1/3 - 2 \times \log 2/3)$$

$$= 15.876 \text{ J mole}^{-1} \text{ K}^{-1}$$

($x_{N_2} = 1/3$ and $x_{O_2} = 2/3$ being the molar fractions of N_2 and O_2).

3. One mole of argon, taken at $T_{Ar} = 293 \text{ K}$, was mixed with two moles of nitrogen, taken at $T_{N_2} = 323 \text{ K}$. The initial pressures of the components and the final pressure of the mixture are equal. Calculate the temperature component of the entropy of mixing. The heat capacities of argon and nitrogen are $C_P^{Ar} = 20.8 \text{ J mole}^{-1} \text{ K}^{-1}$ and $C_P^{N_2} = 29.4 \text{ J mole}^{-1} \text{ K}^{-1}$.

Solution. The gas mixing process is irreversible, which is why the total increase in the system's entropy should be calculated as the sum of changes in the components' entropies, resulting from the rise in temperature and pressure drop, that is

$$\Delta S_{mix} = (\Delta S_{N_2} + \Delta S_{Ar})_{\text{chang. } T} + (\Delta S_{N_2} + \Delta S_{Ar})_{\text{chang. } P}$$

The term $(\Delta S_{N_2} + \Delta S_{Ar})_{\text{chang. } T}$ is the temperature component of the total increase in entropy as a result of mixing. According to Eq. (7.5),

$$(\Delta S_{N_2} + \Delta S_{Ar})_{\text{chang. } T} = C_P^{N_2} 2 \times 2.3 \log (T/T_{N_2}) + C_P^{Ar} 2.3 \log (T/T_{Ar}) \quad (1)$$

in which $C_P^{N_2} = 29.4 \text{ J mole}^{-1} \text{ K}^{-1}$, $C_P^{Ar} = 20.8 \text{ J mole}^{-1} \text{ K}^{-1}$; T is the final temperature of the mixture, calculated using the heat balance equation

$$C_P^{Ar} n_{Ar} (T - T_{Ar}) = C_P^{N_2} n_{N_2} (T_{N_2} - T) \quad (2)$$

where n_{Ar} and n_{N_2} stand for the number of moles of argon and nitrogen, respectively. Substitute numbers into Eq. (2):

$$20.8 \times 1 (T - 293) = 29.4 (323 - T) 2$$

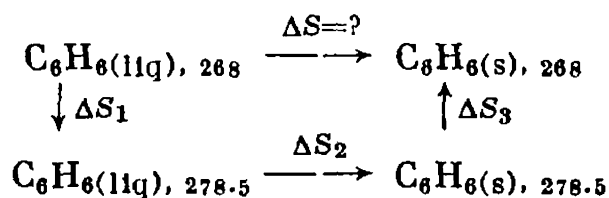
T, K	C_P° , J mole ⁻¹ K ⁻¹	T, K	C_P° , J mole ⁻¹ K ⁻¹	T, K	C_P° , J mole ⁻¹ K ⁻¹
15	2.864	103.0	42.756	160	67.37
20	6.380	103.6	45.486	—	—
25	10.655	—	—	179.6	36.90
30	14.948	105	48.510	192.8	36.99
35	19.664	110	51.87	210.8	37.51
40	23.793	—	55.82	231.4	38.54
45	27.476	120	61.87	250.9	39.75
50	31.055	130	67.33	272.1	41.68
55	34.486	140	71.61	293.9	43.42
60	37.476	150	75.47	—	—
65	40.123	—	78.01	—	—

Transformation of Eq. (2) and calculations give $T = 315$ K. Substitute numbers into Eq. (1):

$$\begin{aligned}\Delta S &= 29.4 \times 2 \times 2.3 \log (315/323) + 20.8 \times 2.3 \log (315/293) \\ &= -1.458 + 1.504 = 0.033 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

4. Calculate the change in entropy during solidification, at 268 K, of one mole of supercooled benzene if at 278 K $\Delta H_m, \text{C}_6\text{H}_6 = 9956$ J/mole, $(C_P)_{\text{C}_6\text{H}_6}^{\text{liq}} = 127.3$ J mole⁻¹ K⁻¹, $(C_P)_{\text{C}_6\text{H}_6}^{\text{s}} = 123.6$ J mole⁻¹ K⁻¹, and $P = \text{const} = 1.01 \times 10^5$ Pa.

Solution. This process is irreversible, therefore it will be mentally conducted reversibly in three steps (see example 2):



Then, $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$.

Calculate the values of ΔS_1 and ΔS_3 according to Eq. (7.5) and that of ΔS_2 according to Eq. (7.14). Then,

$$\begin{aligned}\Delta S &= C_P^{\text{liq}} 2.3 \log \frac{278.5}{268} + \frac{\Delta H_m}{278.5} + C_P^{\text{s}} 2.3 \log \frac{268}{278.5} \\ \Delta S &= 127.3 \times 2.3 \log \frac{278.5}{268} + \frac{9956}{278.5} + 123.6 \times 2.3 \log \frac{268}{278.5} \\ &= 35.89 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

5. Calculate the standard entropy of ethylene if its phase change temperatures and heats are as follows: m.p. = 103.9 K, $\Delta H_m = 3363$ J/mole, b.p. = 169.4 K, and $\Delta H_{\text{evap}} = 13\,595.4$ J/mole. Take into account the temperature dependence of heat capacity, tabulated on p. 82.

Solution. Determine the standard entropy from the equation

$$\begin{aligned}S_{298}^{\text{s}} &= \int_0^{15} \frac{(C_P^{\text{s}})_{\text{C}_2\text{H}_4}}{T} dT + \int_{15}^{103.9} \frac{(C_P^{\text{s}})_{\text{C}_2\text{H}_4}}{T} dT \\ &\quad + \frac{3363.4}{103.9} + \int_{103.9}^{169.4} \frac{(C_P^{\text{liq}})_{\text{C}_2\text{H}_4}}{T} dT + \frac{13\,595.4}{169.4} + \int_{169.4}^{298} \frac{(C_P^{\text{g}})_{\text{C}_2\text{H}_4}}{T} dT\end{aligned}$$

Having converted the above values of C_P^{s} into C_P^{s}/T and plotted $C_P^{\text{s}}/T = f(T)$ (Fig. 10), find the entropy for each temperature range:

(1) by the graphical extrapolation method or using Debye's equation

$$C_P^{\text{s}} = 464.5 \left(\frac{T}{\theta} \right)^3 = kT^3$$

in which θ is the characteristic temperature:

$$S_{15.0}^{\circ} - S_0^{\circ} = 0.966 \text{ J mole}^{-1} \text{ K}^{-1}$$

(2) graphically for the range of 15.0 to 103.9 K:

$$S_{103.9}^{\circ s} - S_{15.0}^{\circ s} = 51.28 \text{ J mole}^{-1} \text{ K}^{-1}$$

(3) for the phase change:

$$\Delta S_m^{\circ} = S_{103.9}^{\circ \text{liq}} - S_{103.9}^{\circ s} = \frac{3363.4}{103.9} = 32.34 \text{ J mole}^{-1} \text{ K}^{-1}$$

(4) graphically for the range of 103.9 to 169.4 K:

$$S_{169.4}^{\circ \text{liq}} - S_{103.9}^{\circ \text{liq}} = 33.22 \text{ J mole}^{-1} \text{ K}^{-1}$$

(5) for the phase change:

$$\Delta S_{\text{evap}}^{\circ} = S_{169.4}^{\circ g} - S_{169.4}^{\circ \text{liq}} = \frac{13595.4}{169.4} = 80.26 \text{ J mole}^{-1} \text{ K}^{-1}$$

(6) graphically for the range of 169.4 to 298 K:

$$S_{298}^{\circ g} - S_{169.4}^{\circ g} = 21.50 \text{ J mole}^{-1} \text{ K}^{-1}$$

(7) the sum of changes in entropy for all temperature ranges will be $S_{298}^{\circ} = 219.62 \text{ J mole}^{-1} \text{ K}^{-1}$.

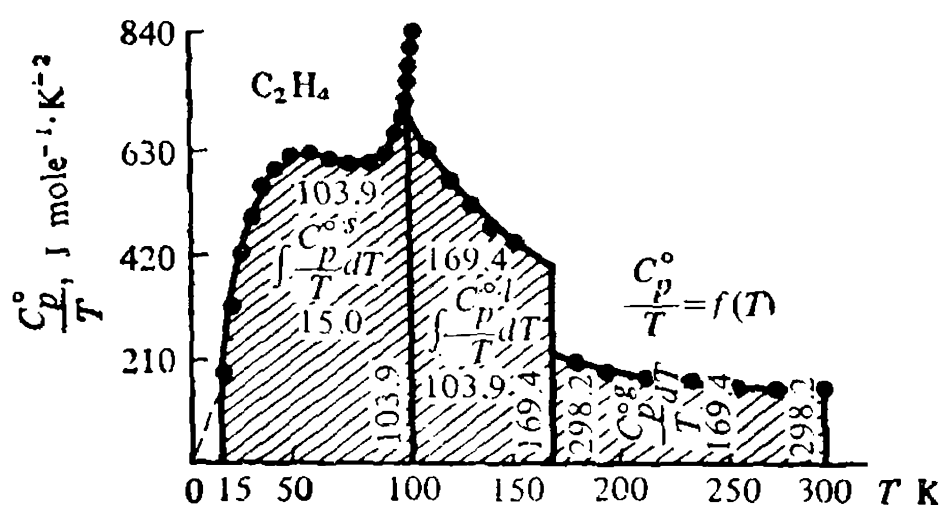


Fig. 10. C_p/T versus temperature in the case of ethylene

6. Calculate the entropy of silver chloride at 870 K.

Solution. According to Eq. (7.15),

$$S_{870, \text{AgCl}}^{\circ} = S_{298, \text{AgCl}}^{\circ} + \sum \int \frac{C_p}{T} dT + \sum \frac{\Delta H_{p.c.}}{T}$$

Take the necessary parameters from handbooks: m.p. = 728 K, $\Delta H_m = 12886.7 \text{ J/mole}$; $C_{\text{AgCl}}^{\text{liq}} = 66.94 \text{ J mole}^{-1} \text{ K}^{-1}$, $S_{\text{AgCl}, 298}^{\circ} = 96.07 \text{ J mole}^{-1} \text{ K}^{-1}$, and $C_p^s = 62.26 + 4.18T - 11.30 \times 10^5/T^2$.

Substitute the numbers into the equation:

$$(S_{870, \text{AgCl}}^{\circ} = 96.07 + \int_{298}^{728} \left(\frac{62.26}{T} + \frac{4.18 \times 10^{-3}}{1} - \frac{11.30 \times 10^5}{T^3} \right) dT \\ + 66.94 \times 2.3 \log \frac{870}{728} + \frac{12\,886.7}{728}$$

After the integration we have

$$S_{870}^{\circ} = 96.07 + 55.55 + 1.80 - 5.309 + 17.70 + 11.92 \\ = 177.70 \text{ J mole}^{-1} \text{ K}^{-1}$$

The increase in the entropy of AgCl due to heating will be

$$(S_{870}^{\circ} - S_{298}^{\circ}) = 81.67 \text{ J mole}^{-1} \text{ K}^{-1}$$

and

$$S_{870, \text{AgCl}}^{\circ} = 177.70 \text{ J mole}^{-1} \text{ K}^{-1}$$

7. Determine the changes in enthalpy, internal energy, and entropy when 2.7 kg of water taken at $P_1 = 1.0133 \times 10^5$ Pa and $T_1 = 298$ K evaporate at $P_2 = 0.50665 \times 10^5$ Pa and $T_2 = 373$ K, $C_P^{\text{liq}} \simeq C_V^{\text{liq}} = 4.187 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$, the specific heat of evaporation being $2260.98 \times 10^3 \text{ J/kg}$. Assume that the resulting water vapour is an ideal gas.

Solution. Changes in the properties of a system do not depend on the course of the process but are determined solely by the initial and final states of the system. Choose any path comprising individual reversible steps, then the change in properties during the process will equal the sum of property changes within each step. Let the process under consideration comprise the following reversible steps: (1) heating of water at $P_1 = 1.0133 \times 10^5$ Pa from $T_1 = 293$ K to $T_2 = 373$ K, (2) transformation of water to vapour (evaporation) at $P_1 = 1.0133 \times 10^5$ Pa and $T_2 = 373$ K, and (3) isothermal expansion of the water vapour at $T_2 = 373$ K from $P_1 = 1.0133 \times 10^5$ Pa to $P_2 = 0.50665 \times 10^5$ Pa. Calculate the change in enthalpy:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_1 = m \int_{293}^{373} C_P^{\text{liq}} dT = 2.7 \times 4.187 \times 10^3 (373 - 293) = 904.392 \times 10^3 \text{ J}$$

$$\Delta H_2 = ml = 2.7 \times 2260.98 \times 10^3 = 6104.646 \times 10^3 \text{ J}$$

$$\Delta H_3 = 0$$

According to the Joule law, the enthalpy and internal energy of an ideal gas at a constant temperature are independent of pressure or

volume. Consequently,

$$\Delta H = 904.392 \times 10^3 + 6104.646 \times 10^3 = 7009.038 \times 10^3 \text{ J}$$

and since $C_P^{\text{liq}} \simeq C_V^{\text{liq}}$,

$$\Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3$$

then

$$\Delta U_1 = \Delta H_1 = 904.392 \times 10^3 \text{ J}$$

$$\Delta U_2 = \Delta H_2 - p\Delta V = \Delta H - P(V_v - V_{\text{liq}})$$

If the volume of the liquid phase is ignored, then

$$\begin{aligned} \Delta U_2 &= \Delta H_2 - pV_v = \Delta H_2 - nRV_2 = 6104.646 \times 10^3 \\ &\quad - \frac{2.7}{18} 8.315 \times 10^3 \times 373 = 5639.419 \times 10^3 \text{ J} \\ \Delta U_3 &= 0 \end{aligned}$$

The change in internal energy during the process under consideration is

$$\Delta U = 904.392 \times 10^3 + 5639.419 \times 10^3 = 6543.811 \times 10^3 \text{ J}$$

and that in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = m \int_{293}^{373} \frac{C_P^{\text{liq}} dT}{T} = mC_P^{\text{liq}} 2.303 \log \frac{T_2}{T_1}$$

$$= 2.7 \times 4.187 \times 10^3 \times 2.303 \log \frac{373}{273} = 3.525 \times 10^3 \text{ J/K}$$

$$\Delta S_2 = \frac{\Delta H_2}{T_2} = \frac{6104.646 \times 10^3}{373} = 16.366 \times 10^3 \text{ J/K}$$

$$\begin{aligned} \Delta S_3 &= nR \ln \frac{P_1}{P_2} = \frac{2.7}{18} 8.315 \times 10^3 \times 2.303 \log \frac{1.0133 \times 10^5}{0.50665 \times 10^5} \\ &= 0.865 \times 10^3 \text{ J mole}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\Delta S = 3.525 \times 10^3 + 16.366 \times 10^3 + 0.865 \times 10^3 = 20.756 \times 10^3 \text{ J/K}$$

8. Find out whether the reaction $\text{Ag} + n\text{Cl}_2 = \text{AgCl}_{(s)} + \left(n - \frac{1}{2}\right)\text{Cl}_2$ is possible at $V = \text{const}$ and 298 K, taking into account the properties of entropy.

Solution. Entropy serves as a criterion of directness of a process only if the latter occurs in an isolated system, therefore mentally conduct the reaction under consideration at $V = \text{const}$ and in the absence of heat exchange with the surrounding medium. To calculate the ΔS of the process assume the following: the reaction is

instantaneous and complete at 298 K; the released heat is expended on heating the excess Cl_2 and solid AgCl ; and the reaction vessel does not absorb the heat. Then, the total change in entropy is the sum of the entropy of the reaction ($\Delta S_{\text{reac}, 298}$) and the entropy of heating of AgCl and Cl_2 (ΔS_{heat}):

$$\Delta S = \Delta S_{\text{reac}} + \Delta S_{\text{heat}}$$

Calculate $\Delta S_{\text{reac}}^\circ$ at 298 K using Eq. (7.13):

$$\Delta S_{\text{reac}}^\circ = S_{\text{AgCl}}^\circ - S_{\text{Ag}}^\circ - \frac{1}{2} S_{\text{Cl}_2}^\circ$$

$$S_{\text{AgCl}}^\circ = 96.07 \text{ J mole}^{-1} \text{ K}^{-1}, \quad S_{\text{Ag}}^\circ = 42.69 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$S_{\text{Cl}_2}^\circ = 223.0 \text{ J mole}^{-1} \text{ K}^{-1}$$

Substitution of the numbers and calculations give $\Delta S_{\text{reac}, 298}^\circ = -57.90 \text{ J mole}^{-1} \text{ K}^{-1}$.

To calculate ΔS_{heat} , first determine the final temperature of $\text{AgCl}_{(\text{liq})}$ and $\text{Cl}_{2(\text{g})}$ from the heat balance equation. The latter is derived assuming that the final temperature of the system is above the melting point of AgCl :

$$\Delta H_{\text{reac}, 298}^\circ = \bar{C}_{\text{AgCl}}^s (T_m - 298) + \Delta H_m + \bar{C}_{\text{AgCl}}^{\text{liq}} (T - T_m) + n_{\text{Cl}_2} \bar{C}_{V, \text{Cl}_2} (T - 298)$$

Assume that the excess of Cl_2 is $n_{\text{Cl}_2} = 5$ moles. The handbooks give $\Delta H_{m, \text{AgCl}} = 12\,886.7 \text{ J mole}^{-1} \text{ K}^{-1}$, $\bar{C}_{\text{AgCl}}^{\text{liq}} = 66.94 \text{ J mole}^{-1} \text{ K}^{-1}$, $\Delta H_{\text{reac}}^\circ = -127\,068 \text{ J/mole}$, $\bar{C}_{\text{AgCl}}^s = 58.99 \text{ J mole}^{-1} \text{ K}^{-1}$, and $\bar{C}_{P, \text{Cl}_2} = 36.36 \text{ J mole}^{-1} \text{ K}^{-1}$;

$$\bar{C}_{V, \text{Cl}_2} = \bar{C}_{P, \text{Cl}_2} - R = 36.36 - 8.314 = 28.04 \text{ J mole}^{-1} \text{ K}^{-1}$$

Substitution of the numbers and calculations give $T = 870 \pm 2 \text{ K}$. Next, calculate the change in entropy during heating:

$$\Delta S_{\text{heat}} = \Delta S_{\text{AgCl}} + \Delta S_{\text{Cl}_2}$$

$$\Delta S_{\text{AgCl}}^\circ = (S_{870}^\circ - S_{298}^\circ) = 81.67 \text{ J mole}^{-1} \text{ K}^{-1}$$

Calculate $\Delta S_{\text{Cl}_2}^\circ$ using Eq. (7.4) and the relation $C_V = C_P - R$:

$$\Delta S^\circ = \int_{298}^{870} \frac{C_V dT}{T} = \int_{298}^{870} \frac{C_P dT}{T} - \int_{298}^{870} \frac{R}{T} dT$$

Compute the integrals:

$$\int_{298}^{870} \frac{C_P dT}{T} = (S_{870}^{\circ} - S_{298}^{\circ}) = 38.28 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\int_{298}^{870} \frac{R}{T} dT = 2.3R \log \frac{870}{298} = 2.3 \times 8.314 \log \frac{870}{298} = 8.895 \text{ J mole}^{-1} \text{ K}^{-1}$$

Substitute the obtained numerical values into the equation to calculate ΔS_{heat} :

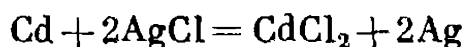
$$\Delta S_{\text{heat}} = 81.67 + 38.28 - 8.895 = 228.6 \text{ J mole}^{-1} \text{ K}^{-1}$$

hence, the total entropy of the process is

$$\Delta S = -57.91 + 228.6 = 170.70 \text{ J mole}^{-1} \text{ K}^{-1}$$

Thus, $\Delta S > 0$. The reaction may take place under the above conditions ($\delta Q = 0$, $T_1 = 298 \text{ K}$, $V = \text{const}$).

9. Determine the change in entropy for the reaction



if it is conducted in a galvanic cell at $1.0133 \times 10^5 \text{ Pa}$ and 298.2 K , the emf of the cell being compensated by that applied externally and equal to 0.6753 V . The standard heats of formation of cadmium chloride and silver are -389.0 and -126.8 kJ/mole , respectively.

Solution. According to Hess' law, the heat of the reaction is

$$\begin{aligned} \Delta H_{298}^{\circ} &= (\Delta H_{f, 298}^{\circ})_{\text{CdCl}_2} - 2 (\Delta H_{f, 298}^{\circ})_{\text{AgCl}} \\ &= -389\,000 - 2(-126\,800) = -135\,400 \text{ J} \end{aligned}$$

Since the reaction is irreversible,

$$\Delta S_{\text{w.g.}} > -135\,400/298.2$$

To calculate $\Delta S_{\text{w.g.}}$ the reaction must be reversed. If it is conducted in a galvanic cell placed in a thermostat where a constant temperature and a constant pressure are maintained and if the emf of the cell E is compensated by an external one, the process will be reversible to all intents and purposes. In this case, $W_{\text{max}} = nFE$, and the heat $Q = T\Delta S$:

$$\Delta U = Q - W_{\text{max}} = Q - (P\Delta V + W'_{\text{max}})$$

or

$$Q = \Delta H + W'_{\text{max}} = \Delta H + nFE$$

Substitution of the values of ΔH_{298}° (the change in enthalpy is independent of the path of the reaction and, therefore, it will be the same irrespective of whether the process is irreversible or not), $n = 1$,

$E = 0.6753$ V, and $F = 96\,487$ C into the last equation gives

$$Q = -135\,400 + 2 \times 0.6753 \times 96\,487 = -5084.7 \text{ J}$$

Hence, $\Delta S_{\text{w.s.}} = -5084.7/298.2 = -17.05 \text{ J mole}^{-1} \text{ K}^{-1}$. The change in entropy for the isolated system as a whole (i.e. the working system plus the thermostat) during the actual process will be

$$\Delta S_{\text{1.s.}} = -17.05 + \frac{235\,400}{298.2} \cdot 437.0 \text{ J mole}^{-1} \text{ K}^{-1}$$

which proves that the process is irreversible.

10. Proceeding from Gibbs' energy, find out whether the reaction $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$ is possible at $P = \text{const} = 1.013 \times 10^5$ Pa and 298 K.

Solution. To solve the problem the sign of ΔG of the reaction must be determined at first. According to Eqs. (7.37) and (7.31):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

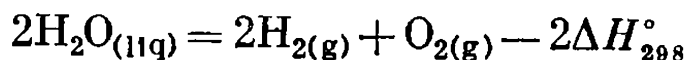
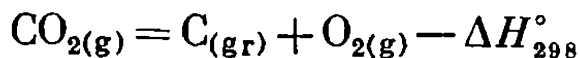
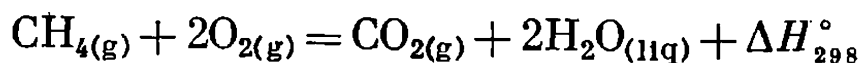
$$\Delta H^\circ = \Delta H_f^\circ, 298 = -127.068 \text{ kJ/mole}$$

$$\Delta S^\circ = S_{\text{AgCl}}^\circ - S_{\text{Ag}}^\circ - \frac{1}{2} S_{\text{Cl}_2}^\circ = -57.97 \text{ J mole}^{-1} \text{ K}^{-1} \text{ (see example 7)}$$

$$\begin{aligned} \Delta G^\circ &= -127.068 - 298(-57.91) = -109\,804.9 \text{ J/mole} \\ &= -109.805 \text{ kJ/mole}, \quad \Delta G^\circ < 0 \end{aligned}$$

Consequently, the reaction is possible.

11. Calculate ΔG_{298}° for the reaction $\text{C}_{(\text{gr})} + 2\text{H}_{2(\text{g})} = \text{CH}_{4(\text{g})}$. Determine ΔH_{298}° from the following thermochemical equations:



Calculate ΔS_{298}° by resorting to Planck's postulate.

Solution. Calculate Gibbs' energy using the equation

$$\Delta G_{298}^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ$$

Use the thermochemical equations to calculate ΔH_{298}° of methane formation:

$$\Delta H_{298}^\circ = \Delta H_{\text{C}_{\text{comb}}}^\circ + 2\Delta H_{\text{H}_2, \text{comb}}^\circ - \Delta H_{\text{CH}_4, \text{comb}}^\circ$$

If $\Delta S_{0\text{K}}^\circ$ for each component of the reaction is known, at absolute zero $\Delta S_{0\text{K}}^\circ$ for the reaction will be

$$\Delta S_{0\text{K}}^\circ = S_{\text{CH}_4}^\circ - S_{\text{C}_{(\text{gr})}}^\circ - 2S_{\text{H}_2}^\circ$$

Calculate the change in entropy for each component from 0 to 298 K:

$$\text{CH}_{4(s, 0\text{K})} = \text{CH}_{4(s, T_m)}, \quad \Delta S_1^\circ = \int_0^{T_m} \frac{(C_P^\circ)_{\text{CH}_4}^s}{T} dT$$

$$\text{CH}_{4(s, T_m)} = \text{CH}_{4(\text{liq}, T_m)}, \quad \Delta S_2^\circ = \frac{\Delta H_{\text{CH}_4}^m}{T_m}$$

$$\text{CH}_{4(\text{liq}, T_m)} = \text{CH}_{4(\text{liq}, T_b)}, \quad \Delta S_3^\circ = \int_{T_m}^{T_b} \frac{(C_P^\circ)_{\text{CH}_4}^{\text{liq}}}{T} dT$$

$$\text{CH}_{4(\text{liq}, T_b)} = \text{CH}_{4(g, T_b)}, \quad \Delta S_4^\circ = \frac{\Delta H_{\text{CH}_4}^{\text{evap}}}{T_b}$$

$$\text{CH}_{4(g, T_b)} = \text{CH}_{4(g, 298)}, \quad \Delta S_5^\circ = \int_{T_b}^{298} \frac{(C_P^\circ)_{\text{CH}_4}^v}{T} dT$$

$$2\text{H}_{2(s, T_m)} = 2\text{H}_{2(s, 0\text{K})}, \quad \Delta S_6^\circ = \int_{T_m}^{0\text{K}} \frac{2(C_P^\circ)_{\text{H}_2}^s}{T} dT$$

$$2\text{H}_{2(\text{liq}, T_m)} = 2\text{H}_{2(\text{liq}, T_m)}, \quad \Delta S_7^\circ = -\frac{2\Delta H_m}{T_m}$$

$$2\text{H}_{2(\text{liq}, T_b)} = 2\text{H}_{2(\text{liq}, T_m)}, \quad \Delta S_8^\circ = \int_{T_b}^{T_m} \frac{2(C_P^\circ)_{\text{H}_2}^{\text{liq}}}{T} dT$$

$$2\text{H}_{2(g, T_b)} = 2\text{H}_{2(\text{liq}, T_b)}, \quad \Delta S_9^\circ = -\frac{2\Delta H_{\text{H}_2}^{\text{evap}}}{T_b}$$

$$2\text{H}_{2(g, 298)} = 2\text{H}_{2(g, T_b)}, \quad \Delta S_{10}^\circ = \int_{298}^{T_b} \frac{2(C_P^\circ)_{\text{H}_2}^g}{T} dT$$

$$\text{C}_{(g, 298)} = \text{C}_{(g, 0\text{K})}, \quad \Delta S_{11}^\circ = \int_{298}^0 \frac{(C_P^\circ)_{\text{C}(g)}}{T} dT$$

$$\text{C}_{(g, 298)} + 2\text{H}_{2(g, 298)} = \text{CH}_{4(g, 298)}, \quad \Delta S_{298}^\circ = \Delta S_{0\text{K}}^\circ + \sum_1^{11} \Delta S^\circ$$

12. Calculate the heat of the reversible process for the reaction $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$. Tabulate the handbook data and the calculation results to demonstrate that ΔG and ΔH are independent of the path taken by the process, whereas the work W' and the amount of

released heat Q depend on it. The maximum useful work $W' = 109\,804.9\text{ J/mole} = 109.805\text{ kJ/mole}$.

Solution. According to Eq. (7.6), $Q_{\text{rev}} = T\Delta S$. According to the handbook data, $\Delta S^\circ = -57.91\text{ J mole}^{-1}\text{ K}^{-1}$.

$$Q_{\text{rev}} = -57.91 \times 298 = 17\,263\text{ J/mole}$$

If we combine Eqs. (7.37), (7.6), and (7.16) into one for P and $T = \text{const}$, the result will be $\Delta H = Q_{\text{rev}} - W'$. Substitution of the numbers gives

$$\Delta H = -17\,263 - 109\,804.9 = -127\,068\text{ J/mole}$$

The work W' of the irreversible process is zero. Tabulate:

Process	$\Delta H_{\text{reac}}^\circ$, J/mole	W' , J/mole	Q , J/mole
Irreversible	127 068	0	127 068
Reversible	127 068	109 805	17 263

It can be seen that the work W' and the heat Q released in the course of the reaction are dependent on the reaction conditions, whereas the change in enthalpy is independent of them.

13. Does a rise in temperature promote the reaction $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$?

Solution. The temperature coefficient of Gibbs' energy for the reaction is given by the equation $\partial\Delta G^\circ/\partial T = -\Delta S^\circ$. The change in entropy is found from the values of the entropies of the substances involved in the reaction. It equals $\Delta S^\circ = -57.91\text{ J/mole}$. Hence, $(\partial\Delta G^\circ/\partial T)_P = 57.91$. Thus, Gibbs' energy increases with temperature, which means that a rise in temperature does not promote the reaction.

14. Two moles of oxygen and one mole of nitrogen were mixed at 298 K. The initial gas pressures $P_{\text{O}_2}^i$ and $P_{\text{N}_2}^i$ as well as the pressure P of the mixture are the same and equal to $1.0133 \times 10^5\text{ Pa}$. The partial pressures of the gases in the mixture, P_{O_2} and P_{N_2} , are 0.668×10^5 and $0.334 \times 10^5\text{ Pa}$, respectively. Calculate ΔG , ΔS , and ΔH for the mixing process.

Solution. Since the gas mixing process is irreversible, substitute it by the sum of the reversible processes occurring under the same (boundary) conditions: $\Delta G = \Delta G_1 + \Delta G_2$, where ΔG_1 and ΔG_2 are the changes in Gibbs' energy for nitrogen and oxygen, due to the pressure changing from $P_{i,1}$ to P_i in the course of mixing.

According to Eq. (7.33),

$$\Delta G_1 = \Delta G_{N_2} = RT \ln (P_{N_2}/P_{N_2}^i), \quad \Delta G_2 = \Delta G_{O_2} = 2RT \ln (P_{O_2}/P_{O_2}^i)$$

Since the initial gas pressures are equal to the final pressure of the mixture, according to Dalton's equation we may write

$$\frac{P_{N_2}}{P_{N_2}^i} = \frac{P_{N_2}}{P} = x_{N_2} = 0.33, \quad \frac{P_{O_2}}{P_{O_2}^i} = \frac{P_{O_2}}{P} = x_{O_2} = 0.67$$

Substitution of the numbers and calculations give

$$\Delta G = RT \, 2.3 (\log x_{N_2} + 2 \log x_{O_2})$$

$$= 8.314 \times 2.3 \times 298 (\log 0.33 + 2 \log 0.67) = -4800 \text{ J/mole}$$

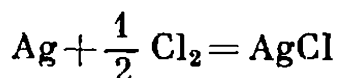
Calculate ΔS in accordance with Eq. (7.26):

$$\begin{aligned} \Delta S &= - \left(\frac{\partial \Delta G}{\partial T} \right)_{P, x} = - RT \ln x_{N_2} - 2RT \ln x_{O_2} \\ &= -16.10 \text{ J mole}^{-1} \text{ K}^{-1} \end{aligned}$$

To calculate ΔH use Eq. (7.21):

$$\begin{aligned} \Delta H &= \Delta G + T\Delta S = RT \ln x_{N_2} + 2RT \ln x_{O_2} \\ &\quad - RT \ln x_{N_2} - 2RT \ln x_{O_2} = 0 \end{aligned}$$

15. Calculate ΔU and ΔA for the reaction



at 298 K and 1.0133×10^5 Pa if $\Delta H_{\text{r, eac}} = -127.159$ kJ/mole and $\Delta n = -0.5$.

Solution. Substitution of the numerical values: $\Delta H = -127.159$ kJ/mole, $\Delta n = -0.5$, and $R = 8.314$ J mole⁻¹ K⁻¹ into Eq. (7.5) gives

$$\Delta U = -127.159 + 0.5 \times 8.314 \times 298 = -125.92 \text{ kJ/mole}$$

Substitution of numerical values into Eq. (7.23) gives

$$\Delta A = -26\,244 + 0.5 \times 8.314 \times 298 = -25.005 \text{ kJ/mole}$$

16. Calculate ΔG° for one mole of NH_3 in a process of isobaric heating ($P = 1.013 \times 10^5$ Pa) from $T_1 = 300$ K to $T_2 = 400$ K if $C_P^\circ = \text{const.}$

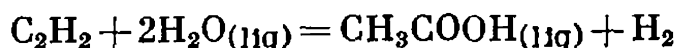
Solution. To calculate ΔG° use Eq. (7.29):

$$\Delta G^\circ = (C_P^\circ - S_{298}^\circ) (400 - 300) - C_P^\circ 400 \times 2.3 \log (400/300)$$

For ammonia $S^\circ = 192.50$ J mole⁻¹ K⁻¹ and $C_P = 35.65$ J mole⁻¹ K⁻¹ at 298 K;

$$\begin{aligned} \Delta G^\circ &= (35.65 - 192.50) (400 - 300) - 35.65 \times 400 \\ &\quad \times 2.3 \log (400/300) = -17.467 \text{ kJ/mole} \end{aligned}$$

17. Determine ΔH° , ΔU° , ΔA° , ΔG° , and ΔS° under standard conditions and at 298.2 K for the reaction



Take the necessary parameters from the handbook.

Solution. Take the entropies and heats of formation of the substances involved in the reaction from the handbook and put them in the following table:

Substance	$\Delta H_f^\circ, 298, \text{ J/mole}$	$S_{298}^\circ, \text{ J mole}^{-1} \text{ K}^{-1}$	$\Delta G_f^\circ, 298 = \Delta H_{298}^\circ - T\Delta S_{298}^\circ, \text{ J/mole}$
$\text{C}_2\text{H}_2(\text{g})$	226.75×10^3	200.8	209.25×10^3
$\text{H}_2\text{O}_{(\text{liq})}$	-285.84×10^3	69.96	-334.46×10^3
$\text{CH}_3\text{COOH}_{(\text{liq})}$	-484.9×10^3	159.8	-576.64×10^3
H_2	0	130.6	0

According to Hess' law, the heat of the reaction is

$$\begin{aligned}\Delta H_{298}^\circ &= \sum (\Delta H_f^\circ, 298)_{\text{r.p.}} - \sum (\Delta H_f^\circ, 298)_{\text{i.s.}} \\ &= (-484.9) - (-2 \times 285.84 + 226.75) 10^3 = 139.97 \times 10^3 \text{ J/mole} \\ \Delta U_{298}^\circ &= \Delta H_{298}^\circ - P\Delta V = \Delta H_{298}^\circ - \Delta nRT\end{aligned}$$

Calculation of Δn is based on the stoichiometric coefficients of gaseous substances only: $\Delta n = n_{\text{H}_2} - n_{\text{C}_2\text{H}_2} = 1 - 1 = 0$. Consequently, $\Delta U_{298}^\circ = \Delta H_{298}^\circ$. Gibbs' energy of the reaction is

$$\begin{aligned}\Delta G_{f, 298}^\circ &= \sum (\Delta G_f^\circ, 298)_{\text{r.p.}} - \sum (\Delta G_{\text{reac}, 298}^\circ)_{\text{i.s.}} \\ &= (-576.64) - (-2 \times 334.46 + 209.25) 10^3 \\ &= -116.97 \times 10^3 \text{ J/mole} \\ \Delta A_{298}^\circ &= \Delta G_{298}^\circ - P\Delta V\end{aligned}$$

For the reaction under consideration, $P\Delta V = 0$. Hence, $\Delta G_{298}^\circ = \Delta A_{298}^\circ$. The entropy of the reaction is

$$\begin{aligned}\Delta S_{298}^\circ &= \sum (S_{298}^\circ)_{\text{r.p.}} - \sum (S_{298}^\circ)_{\text{i.s.}} = (130.6 + 159.8) \\ &\quad - (200.8 + 2 \times 69.96) 10^3 = -50.32 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

Note: r.p. = reaction product; i.s. = initial substances.

18. Calculate ΔG° at 400 K for the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3$. If $\Delta G_{298}^\circ = -16.496 \text{ J/mole}$, the other parameters can be found in the handbook. Assume that $\Delta S^\circ = \text{const.}$

Solution. Calculate the change in Gibbs' energy using Eq. (7.25) according to which

$$\Delta G_T^\circ - \Delta G_{298}^\circ = -\Delta S^\circ \int_{298}^T dT$$

Calculate ΔS° using Eq. (7.13):

$$\Delta S^\circ = S_{\text{NH}_3}^\circ - \frac{1}{2} S_{\text{N}_2}^\circ - \frac{3}{2} S_{\text{H}_2}^\circ, \quad S_{\text{H}_2}^\circ = 192.50$$

$$S_{\text{N}_2}^\circ = 191.5; \quad S_{\text{H}_2}^\circ = 130.6 \text{ J mole}^{-1} \text{ K}^{-1}$$

then $\Delta S^\circ = -99.15 \text{ J mole}^{-1} \text{ K}^{-1}$. Substitution of the numbers and calculations give

$$\Delta G_{400}^\circ = -16.496 + 99.15 \times 100 \times 10^{-3} = -6.581 \text{ kJ mole}^{-1} \text{ K}^{-1}$$

19. Calculate ΔG° at 400 K for the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3$, taking into account the temperature dependence of ΔS .

Solution. Calculate ΔG° by the Tyomkin-Shvartsman method, according to which Eqs. (7.37), (7.33), (7.13a), and (7.32) are combined to give

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ + \int_{298}^T \Delta C_P^\circ dT - \int_{298}^T \frac{\Delta C_P^\circ}{T} dT$$

Substitution of the power series $\Delta C_P^\circ = f(T)$ transforms the equation; the factors dependent on temperature only are denoted as M_0, M_1, M_2, M_{-2} and are found in the handbook:

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - T (\Delta a M_0 + \Delta b M_1 + \Delta c M_2 + \Delta c' M_{-2})$$

The calculation requires the following parameters and their values: $\Delta H_{298}^\circ = -46.19 \text{ kJ/mole}$, $\Delta S_{298}^\circ = -99.15 \text{ J mole}^{-1} \text{ K}^{-1}$, $M_0 = 0.0392$, $M_1 = 13$, $M_{-2} = -3.65 \times 10^7$.

Gas	a	$b \times 10^3$	c	$c' \times 10^{-5}$
N ₂	27.87	4.27	—	—
H ₂	27.28	3.26	—	0.502
NH ₃	29.80	25.48	—	-1.67

$\Delta a = -25.05$, $\Delta b = 18.46 \times 10^{-3}$, $\Delta c' = -2.42 \times 10^5$. Substitution of these numbers into the equation gives

$$\begin{aligned} \Delta G_{400}^\circ &= -46\,190 - 400 (-99.15) - 400 (-25.05 \times 0.0392 \\ &\quad + 18.46 \times 10^{-3} \times 13 + 0.502 \times 10^5 \times 3.65 \times 10^{-7}) \\ &= -6.819 \text{ kJ/mole} \end{aligned}$$

20. Calculate ΔG° for one mole of NH_3 in an isobaric heating process ($P = 1.013 \times 10^5 \text{ Pa}$) from $T_1 = 300 \text{ K}$ to $T_2 = 400 \text{ K}$ if $C_P^\circ = f(T)$.

Solution. Assuming that heat capacity is temperature dependent,

$$C_P^\circ = a + bT + cT^2 + c'/T^2$$

For an individual substance this equation takes the form

$$C_P^\circ = a + bT^2 \quad \text{or} \quad C_P^\circ = a + bT + c'T^{-2}$$

$$S_T^\circ = \int_{T_1}^T \frac{C_T^\circ dT}{T} + S_{T_1}^\circ + \int_{T_1}^T \frac{a dT}{T} + \int_{T_1}^T b dT + \int_{T_1}^T cT dT + \int_{T_1}^T \frac{c'}{T^3} dT + S_{T_1}$$

$$\begin{aligned} S_T^\circ &= a \ln T - a \ln T_1 + bT - bT_1 + \frac{c}{2} T^2 - \frac{c}{2} T_1^2 - \frac{c'}{2T^2} \\ &\quad + \frac{c'}{2T_1^2} + S_{T_1}^\circ = \left(a \ln T + bT + \frac{c}{2} T^2 - \frac{c'}{2T^2} \right) \\ &\quad + \left(S_{T_1}^\circ - a \ln T_1 - bT_1 - \frac{c}{2} T_1^2 + \frac{c'}{2T_1^2} \right) \left(\frac{\partial G}{\partial T} \right)_P = -S \end{aligned}$$

$$\begin{aligned} G_{T_2}^\circ - G_{T_1}^\circ &= -a \int_{T_1}^{T_2} \ln T dT - b \int_{T_1}^{T_2} T dT - \frac{c}{2} \int_{T_1}^{T_2} T^2 dT \\ &\quad + \frac{c'}{2} \int_{T_1}^{T_2} \frac{dT}{T^2} \left(S_{T_1}^\circ - a \ln T_1 - bT_1 - \frac{c}{2} T_1^2 + \frac{c'}{2T_1^2} \right) \int_{T_1}^{T_2} dT \\ &= -aT_2 \ln T_2 + aT_1 \ln T_1 + aT_2 - aT_1 \\ &\quad - \frac{bT_2^2}{2} + \frac{bT_1^2}{2} - \frac{c}{2} \frac{T_2^3}{3} + \frac{c}{2} \frac{T_1^3}{3} + \frac{c'}{2T_2} \\ &\quad - \frac{c'}{2T_1} - \left(S_{T_1}^\circ - a \ln T_1 - bT_1 - \frac{cT_1^2}{2} - \frac{c'}{2T_1^2} \right) (T_2 - T_1) \end{aligned}$$

According to the handbook, $a = 29.80$, $b = 25.48 \times 10^{-3}$, $c = 0$, and $c' = -1.67 \times 10^5 \text{ J mole}^{-1} \text{ K}^{-1}$. Then, the change in Gibbs' energy with temperature will be

$$\begin{aligned} G_{T_2}^\circ - G_{T_1}^\circ &= -29.80 \times 2.3 \log 400 + 29.80 \times 300 \times 2.3 \log 300 \\ &\quad + 29.8 \times 400 - 29.8 \times 300 - \frac{25.48 \times 10^{-3}}{2} 400^2 + \frac{25.48 \times 10^{-3}}{2} 300^2 \\ &\quad - \frac{1.67 \times 10^5}{2 \times 400} + \frac{1.67 \times 10^5}{2 \times 300} \left(192.5 - 29.8 \times 2.3 \log 300 \right. \\ &\quad \left. - 25.48 \times 10^{-3} \times 300 + \frac{1.67 \times 10^5}{2 \times 300^2} \right) (400 - 300) = -71\,341.2 \\ &\quad + 50\,928.2 + 11\,910 - 8940 - 2040 + 1147 - 209 \\ &\quad + 279 - (192.5 - 169.5 - 7.44 + 0.928) 100 = -19\,916 \text{ J/mole} \end{aligned}$$

21. Calculate the pressures at which graphite and diamond are at equilibrium for the temperature range of 298 to 4000 K. In the calculation use the following data for the equilibrium $C_{gr} \rightleftharpoons C_{diam}$:

T, K	$\Delta H^\circ,$ J/mole	$\Delta S^\circ,$ J g ⁻¹ K ⁻¹	$\Delta G^\circ,$ J/mole	$\Delta C_P^\circ,$ J g ⁻¹ K ⁻¹	$\Delta V, \text{cm}^3$
298	18 967.3	-3.364	2903.7	2.602	-1.92
1400	—	-4.853	—	0.418	-1.9

Solution. The negative values of ΔS° and ΔV indicate that the change in temperature does not promote the transformation of graphite to diamond, while an increase in pressure does so. To calculate the equilibrium pressures at elevated temperatures, use the relation $\Delta G_{trans} = f(P, T)$. To this end, write $\Delta G_{P,T}$ as a sum of three addends:

$$\Delta G_{P,T} = \Delta G_{T_1}^\circ + \Delta G_2 + \Delta G_3$$

where $\Delta G_{T_1}^\circ$ stands for the change in Gibbs' energy during transformation of graphite to diamond at 1.0133×10^5 Pa and at temperature T_1 . ΔG_2 is the change ΔG_1 as a result of the increase in temperature from T_1 to T_2 at 1.0133×10^5 Pa, and ΔG_3 is the change ΔG_1 as a result of the increase in pressure from 1.0133×10^5 Pa to P at $T = T_2$. The above conditions occur at $T \leq 1400$ K, which is why we assume that $T_1 = 1400$ K and calculate ΔG_{1400}° . To do this, use Eq. (7.21):

$$\Delta G_{1400}^\circ = \Delta H_{298}^\circ - 1400\Delta S_{298}^\circ - 1400\Delta aM$$

$$\Delta a = \Delta C_P^\circ,_{298}, \quad M = 0.7595$$

and

$$\begin{aligned} \Delta G^\circ &= 1896.6 - 1400(-3.364) - 1400 \times 0.7595(-2.602) \\ &= 9372.16 \text{ J/mole} \end{aligned}$$

Calculate ΔG_P using Eq. (7.25) and assuming that $\Delta G_P = \Delta G_{P,1400} = \text{const.}$ Then,

$$\Delta G_2 = (\Delta C_P^\circ - \Delta S_{1400}^\circ)(T - 1400) - \Delta C_P^\circ T 2.3 \log(T/1400)$$

To calculate ΔG_P also use Eq. (7.31), assuming that $\Delta V = \text{const} = \Delta V_{1400}$. Then, $\Delta G_3 = \Delta V(P - 1) 10.125 \times 10^{-2}$, and the relation $\Delta G = f(P, T)$ takes the form

$$\begin{aligned} \Delta G_{P,T} &= \Delta G_{1400}^\circ + (\Delta C_P^\circ - \Delta S_{1400}^\circ)(T - 1400) \\ &\quad - \Delta C_P^\circ T 2.3 \log \frac{T}{1400} + 10.125 \times 10^{-2} \Delta V(P - 1) \end{aligned}$$

Substitution of the numbers gives

$$\Delta G_{P,T} = 9372.16 + 4.435(T - 1400) + 0.962T \log \frac{T}{1400} - 19.20 \times 10^{-2}P$$

In the state of equilibrium, $\Delta G_{P,T} = 0$. This condition is used to calculate the equilibrium pressure P . Tabulation of the ΔG_T° and P calculation results gives

T , K	298	1400	2400	3400	4000
ΔG_T° , J	2903.7	9372.2	14 346.9	19 501.6	22 656.4
$P \times 10^{-8}$, Pa	15.3	49.35	75.7	102.9	119.57

Thus, diamond is more stable than graphite in the region of low temperatures and high pressures.

Problems

1. An ideal Carnot engine operating at temperatures ranging from 200 to 300 K converts 83.8 J of heat into work. What is the amount of heat transferred to the vessel at 200 K?

2. What amount of heat will be converted into work by an ideal Carnot engine operating at a temperature between 200 and 100 K if it receives the same amount of heat at 200 K as the engine in Problem 1 at 300 K? Explain the difference in the work produced by the ideal engine.

3. At the initial temperature of 348.2 K, one mole of H_2 expands isothermally at first to twice the original volume in a Carnot cycle, then to four times the original volume so that the subsequent adiabatic compression brings it back to the initial volume. Calculate the work for each part of the cycle and the cycle efficiency ($\gamma = 1.4$).

4. Calculate the change in entropy during heating of 16 kg of O_2 from 273 to 373 K: (1) at a constant volume and (2) at a constant pressure. Assume that oxygen is an ideal gas.

5. Calculate the change in entropy during heating of 58.82 kg B_2O_3 from 298 to 700 K, the heat capacity of B_2O_3 is $C_P^\circ = 36.5525 + 106.345 \times 10^{-3} T$ [J mole⁻¹ K⁻¹].

6. Bromobenzene boils at 429.8 K, and the heat of its evaporation at this temperature is 241.9×10^3 J/kg. Calculate the change in entropy during evaporation of 10 kg of bromobenzene.

7. 2×10^{-3} m³ of argon is heated at a pressure of 19.6×10^4 Pa (2 kg/cm²) until its volume increases to 12×10^{-3} m³. What is the change in entropy if the initial temperature is 373 K?

8. Calculate the change in entropy during cooling of 12×10^{-3} kg (12 g) of oxygen from 290 down to 233 K with a simultaneous increase in pressure from 1.01×10^5 to 60.6×10^5 Pa if $C_P^\circ = 32.9$ J mole⁻¹ K⁻¹.

9. Calculate the change in entropy during mixing of 5 kg of water at $T_1 = 353$ K with 10 kg of water at $T_2 = 290$ K. Assume that the

heat capacity of water is constant and equal to $4.2 \text{ J mole}^{-1} \text{ K}^{-1}$.

10. Calculate the total increase in entropy during mixing of $100 \times 10^{-6} \text{ m}^3$ of oxygen with $400 \times 10^{-6} \text{ m}^3$ of nitrogen at 280 K and $1.01 \times 10^5 \text{ Pa}$. $V = \text{const}$.

11. Determine the change in entropy during mixing of one mole of argon at $T_{\text{Ar}} = 293 \text{ K}$ and $P_{\text{Ar}}^\circ = 1.0133 \times 10^5 \text{ Pa}$ with two moles of nitrogen at $T_{\text{N}_2} = 323 \text{ K}$ and $P_{\text{N}_2}^\circ = 1.0133 \times 10^5 \text{ Pa}$. The pressure of the mixture is $P_{\text{mix}} = 1.0133 \times 10^5 \text{ Pa}$. Assume that argon and nitrogen are ideal gases, the heat capacity of each being constant within the above temperature range and equal to $20.935 \text{ J mole}^{-1} \text{ K}^{-1}$ for nitrogen and $12.561 \text{ J mole}^{-1} \text{ K}^{-1}$ for argon.

12. One of two vessels of equal capacity which is 3 m^3 contains 28 kg of nitrogen and the other, 32 kg of oxygen, the temperature in both vessels being the same. Calculate the change in entropy during diffusion after the contents of the vessels are brought in contact. Assume that oxygen and nitrogen are ideal gases.

13. Determine the changes in enthalpy, internal energy, and entropy during transformation of 2.7 kg of water taken at $P_1 = 1.0133 \times 10^5 \text{ Pa}$ and $T_1 = 293 \text{ K}$ to vapour at $P_2 = 0.50665 \times 10^5 \text{ Pa}$ and $T_2 = 373 \text{ K}$. Assume that $C_P^{\text{liq}} \approx C_V^{\text{liq}} = 4.187 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$. The specific heat of evaporation is $2260.98 \times 10^3 \text{ J/kg}$. Assume that the vapour is an ideal gas.

14. Determine the change in entropy during evaporation at 390 K of $100 \times 10^{-3} \text{ kg}$ of water taken at 273 K. The specific heat of water evaporation at 373 K is $2263.8 \times 10^3 \text{ J/kg}$, the specific heat capacity of liquid water is $4.2 \text{ J kg}^{-1} \text{ K}^{-1}$, and the specific heat capacity of water vapour at a constant pressure is $2.0 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$.

15. The molar heat capacity of gaseous methane is given by the equation $C_P = 17.518 + 60.69 \times 10^{-3} T \text{ J mole}^{-1} \text{ K}^{-1}$. The standard entropy of methane at 298 K is $167.73 \text{ J mole}^{-1} \text{ K}^{-1}$. Determine the entropy of $1 \times 10^{-3} \text{ m}^3$ of methane at 800 K and $1.01 \times 10^5 \text{ Pa}$.

16. Find the entropy of the alcohol $\text{C}_2\text{H}_5\text{OH}$ in the tables and calculate the entropy of its vapour at 351 K and $5.05 \times 10^3 \text{ Pa}$, assuming that $\Delta H = 40\,950 \text{ J/mole}$. The temperature dependence of the molar heat capacity is given by the equation

$$C_P = 19.07 + 212.7 \times 10^{-3} T - 108.6 \times 10^{-6} T^2 + 21.9 T^3$$

Name the process in which the change in entropy is maximum.

17. $2 \times 10^{-3} \text{ m}^3$ of helium is mixed with $2 \times 10^{-3} \text{ m}^3$ of argon at 300 K and $1.01 \times 10^5 \text{ Pa}$. After isothermal mixing the gas mixture is heated to 600 K at a constant volume. Calculate the total increase in entropy taking into account that $C_V = 12.6 \text{ J mole}^{-1} \text{ K}^{-1}$ and is independent of temperature.

18. Calculate the change in entropy in the reaction $\text{Pb} + 2\text{AgCl} = \text{PbCl}_2 + 2\text{Ag}$ if corresponding to this reaction in a galvanic cell at 298.2 K is $E = 0.4900 \text{ V}$, and the heats of PbCl_2 and AgCl for-

mation are, respectively, $-357\,732$ and $-126\,775.2$ J/mole. What is the entropy of lead at 298.2 K if $S_{\text{AgCl}}^\circ = 96.23$ J mole $^{-1}$ K $^{-1}$, $S_{\text{PbCl}_2}^\circ = 136.4$ J mole $^{-1}$ K $^{-1}$, and $S_{\text{Ag}}^\circ = 42.68$ J mole $^{-1}$ K $^{-1}$? Calculate the change in entropy when the reaction is conducted in an isolated system.

19. Find the change in entropy during isothermal ($T = 353.2$ K) compression of benzene vapour from $P_1 = 4.0532 \times 10^4$ to $P_2 = 1.0133 \times 10^5$ Pa with subsequent condensation and cooling of liquid benzene to $T = 333.2$ K if $\Delta H_v = 30\,877.92$ J/mole and $(C_P)_{\text{C}_6\text{H}_6} = 1.80$ J g $^{-1}$ K $^{-1}$. Assume that benzene vapour is an ideal gas.

20. Determine the standard change in entropy at 298 K for the following reactions:



For the necessary parameters, see the handbook.

21. One kg of snow at 263 K was placed in a thermally insulated vessel containing 5 kg of water at 303 K. Determine the increase in entropy if the heat of fusion of snow is 334.6×10^3 J/kg, its heat capacity is 2.024×10^3 J kg $^{-1}$ K $^{-1}$, and the heat capacity of water is 4.2×10^3 J kg $^{-1}$ K $^{-1}$.

22. Methylamine hydrochloride $\text{CH}_3\text{NH}_2\text{HCl}$ exists in several crystal modifications. Calculate the heat of its phase change whereby the substance passes from its β -form into the γ -form at 220.4 K; at 19.5 K, $C_P^\gamma = 5.989$ J mole $^{-1}$ K $^{-1}$, the heat capacity of the β -form at 12 K is $C_P^\beta = 8.48$ J mole $^{-1}$ K $^{-1}$, and

$$\Delta S^\beta = \int_{12}^{220.4} C_P^\beta d \ln T = 93.769 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\Delta S^\gamma = \int_{19.5}^{220.4} C_{P(T)} d \ln T = 100.3 \text{ J mole}^{-1} \text{ K}^{-1}$$

Remember that the heat capacity of $\text{CH}_3\text{NH}_2\text{HCl}$ at temperatures ranging from 0 to 20 K obeys Debye's equation $C_P = 464.5 (T/\theta)^3$.

23. At different temperatures, the heat capacity of SO_2 has the following values:

T , K	15.20	25.67	34.87	47.16	60.85
C_P , J mole $^{-1}$ K $^{-1}$	3.612	12.028	20.248	29.106	36.653
T , K	76.98	98.30	120.37	140.92	162.03
C_P , J mole $^{-1}$ K $^{-1}$	42.462	47.71	52.164	55.944	60.732
T , K	192.03	201.74	240.09	260.86	
C_P , J mole $^{-1}$ K $^{-1}$	67.872	88.074	87.318	86.898	

The melting point of SO_2 is 197.64 K, the heat of fusion is $7.4298 \times 10^3 \text{ J/mole}$, the boiling point is 263.08 K, and the heat of evaporation is $24.9336 \times 10^3 \text{ J/mole}$. Calculate the entropy of gaseous SO_2 at 263.08 K and $1.01 \times 10^5 \text{ Pa}$.

24. Graphically calculate the entropy of silver at 473 K, proceeding from the following data:

$T, \text{ K}$	13.5	17.0	26.9	35.0	39.1
$C_V, \text{ J mole}^{-1} \text{ K}^{-1}$	0.462	0.882	3.517	6.657	8.039
$T, \text{ K}$	42.9	45.5	51.4	53.8	77.0
$C_V, \text{ J mole}^{-1} \text{ K}^{-1}$	9.295	10.174	11.756	12.435	17.04
$T, \text{ K}$	100	200	273	535	589
$C_V, \text{ J mole}^{-1} \text{ K}^{-1}$	19.62	23.466	24.158	24.702	24.786

Compare the entropy of silver at 298 K with the value given in the handbook.

25. A solid substance has a melting point at which it turns to a liquid, with a certain amount q of heat being irreversibly transferred in the process. Will it be correct to assume that for this process $\Delta S = q/T_m$? If this assumption is correct, why and on what basis has the fact that the process is irreversible been refuted? If the assumption is wrong, what is the right expression for ΔS ?

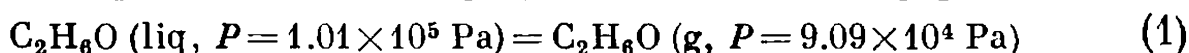
26. Two similar vessels (each having volume V) communicate through a tube with a stopcock. The material of which the system is made is a perfect thermal insulator. At first, n moles of a monatomic Van der Waals gas were placed in one of the vessels at temperature T_0 , while the other vessel remained empty, then the stopcock was opened for equilibrium to be established in the system. Assume that the gas had a heat capacity ($C_V = \frac{3}{2}R$) of an ideal gas. Determine Q , W , ΔU , ΔA , and ΔS , given n , V , T_0 , the Van der Waals constants a and b , and the universal constants.

27. Why should the use of entropy as a criterion of spontaneity of a process be based on the assumption that $\Delta S_{\text{i.s.}} = \Delta S_{\text{w.s.}} - \Delta S_{\text{s.m.}}$, and why only $\Delta G_{\text{w.s.}}$ (rather than $\Delta G = \Delta G_{\text{w.s.}} - \Delta G_{\text{s.m.}}$) is taken into consideration for Gibbs' energy?

Note: i.s.—isolated system, w.s.—working system, and s.m.—surrounding medium.

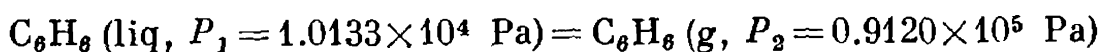
28. Calculate the change in Gibbs' energy during compression of $0.7 \times 10^{-2} \text{ kg}$ of N_2 at 300 K and 5.05×10^4 to $3.031 \times 10^5 \text{ Pa}$, assuming that nitrogen is an ideal gas.

29. Calculate ΔG , if the boiling point is 351 K (assuming that the alcohol vapour is an ideal gas), for the following processes:



What conclusions can be drawn from the obtained results as regards the direction of the processes?

30. Calculate ΔA and ΔG for two moles of benzene in the following isothermal evaporation process:



The normal boiling point is $T_{\text{n.b.}} = 353.3 \text{ K}$.

31. The pressure of saturated vapour over solid benzene at 268.2 K is 2279.8 Pa, and that of saturated vapour over supercooled (liquid) benzene is 2639.7 Pa. Calculate the change in Gibbs' energy in the course of solidification of one mole of supercooled benzene at the above temperature (assuming that the benzene vapour is an ideal gas).

32. The heat of fusion of ice at 273 K is $334.7 \times 10^3 \text{ J/kg}$. The specific heat capacity of water is $4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$, and that of ice is $2.02 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$. Determine ΔG , ΔH , and ΔS for transformation of one mole of supercooled water to ice at 268 K.

33. At 298 K the entropy of rhombic sulphur is $32.04 \text{ J mole}^{-1} \text{ K}^{-1}$, and that of monoclinic sulphur is $32.68 \text{ J mole}^{-1} \text{ K}^{-1}$. The heats of their combustion are, respectively, $-297\,948$ and $-298\,246 \text{ J/mole}$. Calculate ΔG for the reaction $S_{\text{rhomb}} = S_{\text{mon}}$. In the first approximation ignore the difference between the densities of rhombic and monoclinic sulphur. What conclusion can be drawn from the calculation result?

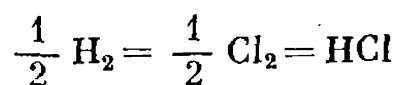
34. Calculate W , ΔH , ΔU , ΔS , ΔA , and ΔG for isothermal compression of one mole of an ideal monatomic gas at 773 K and 5.05×10^3 to $1.01 \times 10^4 \text{ Pa}$.

35. One mole of a gas reversibly and isothermally expands in an isolated system at 273.16 K from 1.01×10^7 to $1.01 \times 10^6 \text{ Pa}$. Calculate W , Q , ΔU , ΔH , ΔS , ΔA , and ΔG (assuming the gas to be ideal): (1) for the gas and the isolated system as a whole, and (2) in the case of free expansion of the gas (expansion in vacuum is irreversible), for the gas and the isolated system as a whole. Tabulate the calculation results.

36. At 298.2 K and $1.01 \times 10^5 \text{ Pa}$ the molar entropy of diamond is 2.457 J/K , and that of graphite is 5.73 J/K . The heat of diamond's combustion is 387.9 J/mole , and that of graphite's combustion is 382.2 J/mole . The densities of diamond and graphite are 3.513×10^3 and $2.26 \times 10^3 \text{ kg/m}^3$, respectively. Calculate ΔH° for the transformation of diamond to graphite at 298.2 K and $1.01 \times 10^5 \text{ Pa}$. Which of the two forms—graphite or diamond—is stable under the above conditions? Can another stable form be obtained if the pressure is raised? If yes, how high must the pressure be?

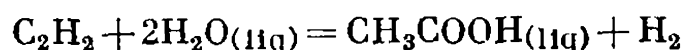
37. Determine the standard change in Gibbs' energy at 298 K for the reaction $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$. The values of ΔH_{298}° and S_{298}° can be found in the handbook.

38. Derive the temperature dependence of ΔG_T° for the reaction



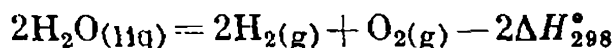
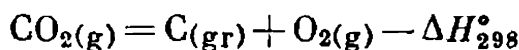
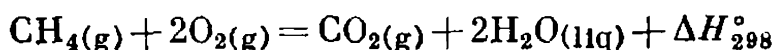
The values of ΔH_{298}° , ΔG_{298}° , and $C_P = f(T)$ can be found in the handbook.

39. Determine ΔH° , ΔU° , ΔA° , ΔC° , and ΔS° at 298.2 K for the reaction



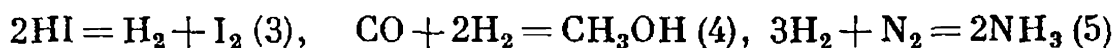
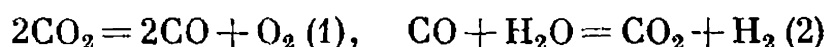
Find the necessary data in the handbook.

40. Calculate ΔG_{298}° for the reaction $\text{C}_{(\text{gr})} + 2\text{H}_{2(\text{g})} = \text{CH}_{4(\text{g})}$, ΔH_{298}° being determined from the following thermochemical equations:



Calculate ΔS_{298}° using Planck's postulate.

41. Calculate ΔG_{700}° for the following reactions:



Find the values of ΔH_{298}° , S_{298}° , and $C_P = f(T)$ in the handbook.

42. Determine the changes in U , H , S , A , and G , as well as the final V and T during adiabatic expansion of $1 \times 10^{-3} \text{ m}^3$ of oxygen, taken at 298.2 K and $5.065 \times 10^5 \text{ Pa}$, to $1.013 \times 10^5 \text{ Pa}$. The molar heat capacity of oxygen at a constant pressure is $20.63 \text{ J mole}^{-1} \text{ K}^{-1}$, and the molar entropy at 298.2 K and $1.013 \times 10^5 \text{ Pa}$ is $206 \text{ J mole}^{-1} \text{ K}^{-1}$.

43. Prove whether ethylene will react with water at 298 K and $1.013 \times 10^5 \text{ Pa}$.

44. Prove whether hydrogen will react with oxygen at 180 K and $1.013 \times 10^5 \text{ Pa}$.

45. Prove whether nitrogen will react with hydrogen at 700 K and $1.013 \times 10^5 \text{ Pa}$.

46. For the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3$,

$$\Delta G_T^\circ = 43\,540 + 29.7T \log T + 15.87 \times 10^{-3}T^2$$

Calculate ΔS_{298}° proceeding from the above data and compare the result with the values given in the handbook.

47. For the reaction $2\text{H}_2 + \text{S}_2 = 2\text{H}_2\text{S}$,

$$\Delta G_T^\circ = 168\,350 + 30.35T \log T - 5.07 \times 10^{-3}T^2$$

Calculate ΔS_{298}° proceeding from the above data and compare the result with the values given in the handbook.

Multivariate Problems

1. Calculate the change in entropy during heating (cooling) of g kg of substance A at a constant pressure and temperatures ranging from T_1 to T_2 , if the melting and boiling points of the substance are known along with its heat capacity in the solid, liquid, and gaseous states as well as the heats of its fusion and evaporation*.

Variant	Substance A	g , kg	T_1 , K	T_2 , K
1	Br_2 , bromine	25	373	173
2	H_2O , water	45	421	223
3	Hg, mercury	40	193	673
4	CCl_4 , carbon tetrachloride	80	323	373
5	CH_2O_2 , formic acid	10	393	273
6	$\text{C}_2\text{HCl}_3\text{O}_2$, trichloroacetic acid	15	160	350
7	CH_4O , methanol	80	303	473
8	$\text{C}_2\text{H}_3\text{ClO}_2$, chloroacetic acid	15	423	313
9	$\text{C}_2\text{H}_4\text{O}_2$, acetic acid	8	423	223
10	$\text{C}_2\text{H}_6\text{O}$, ethanol	50	373	143
11	$\text{C}_3\text{H}_6\text{O}$, acetone	10	173	373
12	$\text{C}_4\text{H}_{10}\text{O}$, ethyl ether	50	143	323
13	C_5H_{12} , <i>n</i> -pentane	35	323	133
14	C_6H_6 , benzene	1	383	273
15	C_6H_{12} , cyclohexane	100	373	273
16	C_6H_{14} , <i>n</i> -hexane	10	173	373
17	C_7H_8 , toluene	50	423	173
18	$\text{C}_7\text{H}_9\text{N}$, <i>p</i> -methylaniline	40	523	303
19	C_{10}H_8 , naphthalene	25	328	523
20	$\text{C}_{10}\text{H}_8\text{O}$, α -naphthol	75	579	323
21	C_8H_{10} , <i>o</i> -xylene	60	423	223

* The mean heat capacities of substances in all states of aggregation, the heats of their fusion and evaporation can be found in the handbook. Ignore the heats of transfer from one modification to another. If the appropriate data cannot be found in the handbook, assume that the heat capacities are independent of temperature. If the handbook does not contain a particular heat capacity, calculate it approximately using the data in the handbook.

2. Determine ΔS , ΔU , ΔH , ΔA , and ΔG for mixing V_A m³ of gas A with V_B m³ of gas B at $T = 298$ K. The initial pressure of the gases is 1.01×10^5 Pa. The final volume of the mixture is $V_f = V_A + V_B$. The gases and their volumes are tabulated below.

Variant	Gas A	$V_A \times 10^4$, m ³	T_A , K	Gas B	$V_B \times 10^4$, m ³	T_B , K	P , Pa
1	H ₂	1	303	N ₂	2	290	101 325
2	H ₂ O	5	388	O ₂	6	310	101 325
3	He	7	275	CO ₂	8	290	131 722
4	He	1	277	H ₂	5	303	303 975
5	CH ₄	7	268	C ₂ H ₆	9	288	172 252
6	CH ₄	2	298	Ne	3	283	303 975
7	CO	3.3	268	C ₂ H ₆	4	300	70 927
8	CO ₂	6	280	N ₂	7	310	141 855
9	CO ₂	7	258	CO	9	278	40 530
10	CO ₂	2	303	CH ₄	4	289	810 060
11	C ₂ H ₆	3	268	Xe	6	296	206 450
12	C ₂ H ₆	8	313	CH ₄	9	289	151 987
13	N ₂	7	280	Cl ₂	9	299	192 517
14	N ₂	4	293	H ₂ O	7	383	101 325
15	O ₂	6	333	N ₂	8	297	506 625
16	O ₂	1	333	H ₂	4	290	101 325
17	O ₂	1	303	Ar	3	298	101 325
18	F ₂	4	281	Cl ₂	5	292	182 385
19	Ne	1	278	N ₂	8	296	50 662
20	Cl ₂	5	243	N ₂	7	278	50 662
21	Cl ₂	1	308	Ar	7	292	253 312
22	Ar	1	276	He	6	291	151 987
23	Kr	2	276	CO ₂	6	288	121 590
24	Kr	2	278	CO	7	308	40 530
25	Xe	3	263	F ₂	6	286	172 252

3. Calculate the increase in entropy during mixing of V_A m³ of gas A at temperature T_A , K, with V_B m³ of gas B at temperature T_B , K. The process occurs at $V = \text{const.}$ Assume that the substances behave as ideal gases, their initial pressure being 1.013×10^5 Pa and the final pressure of the mixture being P (refer to the above table).

4. Calculate ΔS for the processes in which one mole of gas A passes from state 1 ($P_1 = 1.013 \times 10^5$ Pa, $T_1 = 298$ K) into state 2 (P_2 , T_2).

Variant	Gas A	$P_2 \times 10^{-2}$, Pa	T_2 , K	Variant	Gas A	$P_2 \times 10^{-2}$, Pa	T_2 , K	Variant	Gas A	$P_2 \times 10^{-2}$, Pa	T_2 , K
1	H ₂	1.33	250	10	CO ₂	13.33	750	18	F ₂	13.33	400
2	H ₂ O	13.3	350	11	C ₂ H ₆	133.30	800	19	Ne	133.3	450
3	He	133.0	400	12	C ₂ H ₆	1333	850	20	Cl ₂	1333	500
4	He	1330	450	13	N ₂	1.33	900	21	Cl ₂	1.33	550
5	CH ₄	1.33	500	14	N ₂	13.33	950	22	Ar	13.33	600
6	CH ₄	13.3	550	15	O ₂	133.3	1000	23	Kr	133.3	650
7	CO	133	600	16	O ₂	1333	250	24	Kr	1333	700
8	CO ₂	1330	650	17	O ₂	1.33	350	25	Xe	1.33	750
9	CO ₂	1.3	700								

5. Determine the changes in the following functions: (1) ΔS and ΔG at $P = \text{const}$, (2) ΔS and ΔA during heating of a gas by 100° ($V = \text{const}$). For gas characteristics, see Problem 3.

6. There are two vessels isolated from the surrounding medium. One vessel contains n_1 moles of substance A in the solid state and n_2 moles in the liquid state at the melting point, while the other vessel contains n_1 moles of substance B in the solid state and n_2 moles in the liquid state at the melting point. Both vessels are made to communicate. Determine the direction of the process which will be initiated in the system and establish which substance—A or B—will melt or solidify. Describe the conditions under which the system will reach the state of equilibrium (T , n_1 , n_2). Calculate the change in entropy during transition of the system from the initial state to that of equilibrium. Is this process reversible or not? Base your calculations on the data on p. 106 and those given in the handbook.

7. Calculate W , ΔU , ΔH , and ΔS for the processes in which an ideal gas passes from state 1 (P_1 , T_1) into state 2 (P_2 , T_2): with (1) isothermal expansion and isobaric heating, (2) isothermal expansion and isochoric heating, (3) adiabatic expansion and isobaric heating, and (4) adiabatic expansion and isochoric heating.

Variant	State 1		State 2		Variant	State 1		State 2	
	P_1 , Pa	T_1 , K	P_2 , Pa	T_2 , K		P_1 , Pa	T_1 , K	P_2 , Pa	T_2 , K
1	101 325	273	506 625	540	6	202 650	300	121 590	700
2	101 325	273	60 795	560	7	243 180	300	162 120	600
3	84 060	285	40 530	600	8	263 445	285	182 385	700
4	121 590	298	70 927	590	9	172 252	298	162 120	500
5	151 987	280	81 060	600	10	162 120	300	81 060	400

Vari- ant	Substance		Vari- ant	Substance		n ₁	n ₂
	A	B		A	B		
1	H ₂ O	CH ₃ COOH	14	C ₃ H ₅ (OH) ₃	CH ₃ COOH	0.4	0.6
2	H ₂ O	C ₃ H ₅ (OH) ₃	15	HCOOH	C ₃ H ₅ (OH) ₃	0.4	0.6
3	H ₂ O	(CH ₂) ₆	16	HCOOH	CH ₃ COOH	0.3	0.7
4	H ₂ O	HCOOH	17	HCOOH	(CH ₂) ₆	0.7	0.3
5	H ₂ O	C ₆ H ₅ NH ₂	18	CH ₃ COOH	(CH ₂) ₆	0.4	0.6
6	C ₆ H ₆	H ₂ O	19	C ₃ H ₇ COOH	n-C ₈ H ₄ (CH ₃) ₂	0.3	0.7
7	C ₆ H ₆	CH ₃ COOH	20	C ₃ H ₇ COOH	CH ₃ COOH	0.4	0.6
8	C ₆ H ₆	(CH ₂) ₆	21	C ₃ H ₇ COOH	(CH ₂) ₆	0.2	0.8
9	C ₆ H ₆	C ₃ H ₅ (OH) ₃	22	C ₃ H ₇ COOH	HCOOH	0.6	0.4
10	C ₆ H ₆	HCOOH	23	C ₃ H ₇ COOH	C ₆ H ₆	0.7	0.3
11	n-C ₆ H ₄ (CH ₃) ₂	CH ₃ COOH	24	C ₃ H ₇ COOH	C ₃ H ₅ (OH) ₃	0.5	0.5
12	C ₃ H ₅ (OH) ₃	n-C ₆ H ₄ (CH ₃) ₂	25	C ₃ H ₇ COOH	C ₆ H ₅ COOH	0.1	0.9
13	C ₃ H ₅ (OH) ₃	(CH ₂) ₃					

8. Calculate ΔH , ΔU , ΔS , and ΔG for the following processes:

Variant	Process, conditions
1	$\text{H}_2\text{O (liq, 273 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (s, 273 K, } P=1.01 \times 10^5 \text{ Pa)}$
2	$\text{H}_2\text{O (s, 273 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (s, 263 K, } P=1.01 \times 10^5 \text{ Pa)}$
3	$\text{H}_2\text{O (liq, 263 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (liq, 273 K, } P=1.01 \times 10^5 \text{ Pa)}$
4	$\text{H}_2\text{O (s, 263 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (liq, 263 K, } P=1.01 \times 10^5 \text{ Pa)}$
5	$\text{H}_2\text{O (liq, 298 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (liq, 373 K, } P=1.01 \times 10^5 \text{ Pa)}$
6	$\text{H}_2\text{O (liq, 373 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (g, 373 K, } P=1.01 \times 10^5 \text{ Pa)}$
7	$\text{Ideal gas (298 K, } P=1.01 \times 10^7 \text{ Pa)} = \text{Ideal gas (298 K, } P=1.01 \times 10^5 \text{ Pa)}$
8	$\text{Ideal gas (298 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{Ideal gas (298 K, } P=1.01 \times 10^5 \text{ Pa)}$
9	$\text{H}_2\text{O (liq, 298 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (g, 298 K, } P=3.03 \times 10^3 \text{ Pa)}$
10	$\text{C}_6\text{H}_6 \text{ (liq, 353.1 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{C}_6\text{H}_6 \text{ (g, 353.1 K, } P=0.9 \times 10^5 \text{ Pa)}$
11	$\text{C}_6\text{H}_6 \text{ (liq, 353.1 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{C}_6\text{H}_6 \text{ (g, 353.1 K, } P=1.01 \times 10^5 \text{ Pa)}$
12	$\text{C}_6\text{H}_6 \text{ (liq, 353.1 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{C}_6\text{H}_6 \text{ (g, 353.1 K, } P=1.1 \times 10^5 \text{ Pa)}$
13	$\text{H}_2\text{O (liq, 373 K, } P=1.01 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (g, 373 K, } P=0.8 \times 10^5 \text{ Pa)}$
14	$\text{H}_2\text{O (liq, 298 K, } P=1.1 \times 10^5 \text{ Pa)} = \text{H}_2\text{O (g, 298 K, } P=1.1 \times 10^6 \text{ Pa)}$

Draw an appropriate conclusion from the obtained results as regards the direction of the process.

9. When a substance (whose vapour behaves as an ideal gas) passes from the liquid into the gaseous state at temperature T and a pressure of $1.01 \times 10^5 \text{ Pa}$, the heat of evaporation is expended. Assume that this heat is independent of temperature. Calculate the changes in entropy, Gibbs' energy, Helmholtz' energy, internal

Variant	T, K	Sub- stance A	Variant	T, K	Sub- stance A	Variant	T, K	Sub- stance A
1	20.4	H ₂	10	283	CS ₂	18	20	Ne
2	283	H ₂ O	11	273	C ₂ N ₂	19	4	He
3	293	HCN	12	251	CNCl	20	262	SO ₂
4	202	H ₂ S	13	73	N ₂	21	231	Cl ₂
5	189	HCl	14	239.7	NH ₃	22	85	F ₂
6	190	HBr	15	121	NO	23	210	Br ₂
7	236	HI	16	184	N ₂ O	24	122	Kr
8	81	CO	17	85	O ₂	25	165	Xe
9	194	CO ₂						

energy, enthalpy, and the work of expansion of one mole of the substance in this process. Determine the changes in these functions if the vapour of one mole of the substance A is heated from temperature T to $T + 25^\circ$ in (a) an isochoric and (b) isobaric manner. What would be the increase in the temperature of the substance, in degrees, if the change in internal energy during transition from the liquid into gaseous state were expressed in terms of increasing temperature? Find the necessary data in the handbook.

CHAPTER 8

Elements of Statistical Thermodynamics

Basic Equations and Symbols

The internal energy of a substance is essentially the sum of the energies of translational motion (U_{trans}), rotational (U_{rot}), internal motion (U_{int}), and molecular interaction ($U_{\text{m.i.}}$):

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{int}} + U_{\text{m.i.}} \quad (8.1)$$

But if the system is in an ideal gaseous state, the energy of each molecule's motion is the sum of the following components:

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{l.r.}} + \varepsilon_{\text{vibr}} + \varepsilon_{\text{el}} + \varepsilon_{\text{nuc}} \quad (8.2)$$

where $\varepsilon_{\text{trans}}$ is the energy of the molecule's translational motion, ε_{rot} is the energy of the molecule's rotation, $\varepsilon_{\text{l.r.}}$ is the energy of rotation of a group of atoms with respect to another within a molecule or, in other words, the energy of internal rotation, $\varepsilon_{\text{vibr}}$ is the energy of vibration of atoms within a molecule, ε_{el} is the energy of motion of the electrons within atoms, and ε_{nuc} is the energy of intranuclear motion.

The internal energy of a substance can be written as follows:

$$U = \sum_i N_i \varepsilon_i \quad (8.3)$$

where N_i is the number of molecules on the i th energy level, and ε_i is the energy on that level. The sum of molecules occupying all energy levels for one mole of the substance equals the Avogadro constant:

$$\sum_i N_i = N_A \quad (8.4)$$

It is more convenient to reckon the internal energy from the energy on the zeroth level. The internal energy on that level includes the energy of intranuclear motion, the energy of the electrons, and the

vibrational energy on the zeroth vibrational quantum level:

$$U - U_0 = U_{\text{trans}} + U_{\text{rot}} + U_{\text{i.r.}} + (U - U_0)_{\text{vibr}} \quad (8.5)$$

The population of every possible energy level is

$$N_i = N_0 e^{-\epsilon_i/kT} \quad (8.6)$$

where N_i is the population of the i th energy level, N_0 is the population of the zeroth energy level, ϵ_i is the energy of the i th energy level, and k is the Boltzmann constant.

Some energy levels are degenerate, that is several levels have the same energy:

$$N_i = \frac{N_0}{g_0} g_i e^{-\epsilon_i/kT} \quad (8.7)$$

where g_0 is the degree of degeneracy of the zeroth energy level, and g_i is that of the i th energy level. In the case of diatomic molecules, the translational motion is not degenerate, and each rotational level is degenerate $(2j + 1)$ times, j being the rotational quantum number; the vibration is not degenerate, and each electron level is degenerate $(2S + 1)$ times, S being the total spin of the molecule. If the degeneracy of the energy levels is taken into account, then

$$N_A = \frac{N_0}{g_0} \sum_i g_i e^{-\epsilon_i/kT} \quad (8.8)$$

If we denote

$$\sum_i g_i e^{-\epsilon_i/kT} = Z \quad (8.9)$$

where Z is the sum over states*,

$$N_0/g_0 = N_A/Z \quad (8.10)$$

Alternatively, Eqs. (8.10) and (8.7) can be written as follows:

$$N_i/N_A = g_i e^{-\epsilon_i/kT} / Z \quad (8.11)$$

where N_i/N_A is the fraction of molecules on the i th energy level. The internal energy of the substance will then be

$$U - U_0 = RT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (8.12)$$

$$Z = \sum_i g_i e^{-\frac{(\epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{i.r.}} + \epsilon_{\text{vibr}} + \epsilon_{\text{el}})_i}{kT}} \quad (8.13)$$

* In the literature, the sum over states is sometimes termed statistical sum or state sum.

According to the multiplicativity rule,

$$Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{t.r.}} Z_{\text{vibr}} Z_{\text{el}} \quad (8.14)$$

The translational component of the sum over the system's states is determined from the equation*

$$Z_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3 N_A} V e \quad (8.15)$$

where m is the mass of the molecule ($m = M/N_A$), h is the Planck constant, k is the Boltzmann constant, N_A is the Avogadro constant, V is the volume of one mole of gas, and e is the natural logarithm base. If the volume is expressed in terms of P and T according to the Mendeleev-Clapeyron equation, then the translational component of the sum over states will be

$$Z_{\text{trans}} = \frac{(2\pi k)^{3/2} R M^{3/2} T^{5/2} P^{-1}}{h^3 N_A^{5/2}} e \quad (8.16)$$

The natural logarithm of the translational component of the sum over states will be

$$\begin{aligned} \ln Z_{\text{trans}} = 2.3026 \log \frac{(2\pi k)^{3/2} R e}{h^3 N_A^{5/2}} + \frac{3}{2} 2.3026 \log M \\ + \frac{5}{2} 2.3026 \log T - 2.3026 \log P \end{aligned} \quad (8.17)$$

If all the constants are expressed in the International System of Units, Eq. (8.17) will take the form

$$\ln Z_{\text{trans}} = 3.4539 \log M + 5.7565 \log T - 2.3026 \log P + 8.8612 \quad (8.18)$$

Taking the logarithm of Eq. (8.15) and expressing the mass of the molecule as the molecular weight will give

$$\begin{aligned} \ln Z_{\text{trans}} = 3.4539 \log M + 3.4539 \log T \\ + 2.3026 \log V + 6.7433 \end{aligned} \quad (8.19)$$

* Rigorous derivation of the equation for the translational component of the sum over states gives

$$Z'_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

The quantity Z'_{trans} in Eq. (8.15) is multiplied by e/N_A because entropy is expressed as the sum over states:

$$S_T = R \ln Z \frac{e}{N_A} + RT \left(\frac{\partial \ln Z}{\partial T} \right)_V$$

The quantity e/N_A forms part of the translational component of the sum over states.

The rotational component of the sum over states for diatomic molecules is

$$Z_{\text{rot}} = \frac{8\pi^2 I k T}{h^2 \sigma} = \frac{k T}{B_e \sigma} \quad (8.20)$$

where I is the molecule's moment of inertia, σ is the degree of symmetry, and B_e is the rotational constant. In the case of homonuclear diatomic molecules, $\sigma = 2$, and in the case of heteronuclear ones, $\sigma = 1$. Substitution of constants in the International System of Units into Eq. (8.20) and taking its logarithm give

$$\ln Z_{\text{rot}} = 2.3026 \log I + 2.3026 \log T - 2.3026 \log \sigma + 104.5265 \quad (8.21)$$

The rotational component of the sum over states for polyatomic molecules is as follows:

for a spherically symmetric top

$$Z_{\text{rot}} = \frac{8\pi^2}{\sigma} \left(\frac{2\pi I k T}{h^2} \right)^{3/2} \quad (8.22)$$

for a symmetric top

$$Z_{\text{rot}} = \frac{8\pi^2}{\sigma} \frac{(2\pi I_A k T)^{1/2}}{h} \frac{2\pi I_B k T}{h^2} \quad (8.23)$$

for an asymmetric top

$$Z_{\text{rot}} = \frac{8\pi^2}{\sigma} \left(\frac{2\pi I_A k T}{h^2} \right)^{1/2} \left(\frac{2\pi I_B k T}{h^2} \right)^{1/2} \left(\frac{2\pi I_C k T}{h^2} \right)^{1/2} \quad (8.24)$$

Taking the logarithms of Eqs. (8.22) through (8.24) and substitution of constants in the International System of Units give

$$\begin{aligned} \ln Z_{\text{rot}} = 2.3026 \log \left[\left(8\pi^2 \left(\frac{2\pi k}{h^2} \right)^{3/2} \frac{1}{\sigma} \right) \right] + 0.5 \times 2.3026 \log (I_A I_B I_C) \\ + \frac{3}{2} \ln T = 0.5 \times 2.3026 \log (I_A I_B I_C) + 3.4539 \log T - 2.3026 \log \sigma \\ + 157.3621 \end{aligned} \quad (8.25)$$

The product of the principal moments of inertia, $I_A I_B I_C$, can be calculated from the secular equation (see Chap. 4)

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} - I_{xy} - I_{xz} \\ -I_{xy} + I_{yy} - I_{yz} \\ -I_{xz} + I_{yz} + I_{zz} \end{vmatrix} \quad (8.26)$$

In the case of polyatomic molecules containing groups of atoms that are capable of rotating one relative to another, the free internal rotational component of the sum over states is calculated using the

equation

$$Z_{i.r.} = \left(\frac{8\pi^3 k T I_{\text{red}}}{h^2} \right)^{1/2} \frac{1}{\sigma} \quad (8.27)$$

in which σ is the degree of symmetry of a group of atoms, and I_{red} is the reduced moment of inertia of internal rotation:

$$I_{\text{red}} = I_1 I_2 / (I_1 + I_2) \quad (8.28)$$

After substitution of constants in the International System of Units into Eq. (8.28) and taking its logarithm we have

$$\begin{aligned} \ln Z_{i.r.} = & 0.5 \times 2.3026 \log \frac{8\pi^3 k}{h^2} + 2.3026 \times 0.5 \log T \\ & + 0.5 \times 2.3026 \log I_{\text{red}} - 2.3026 \log \sigma \end{aligned} \quad (8.29)$$

$$\begin{aligned} \ln Z_{i.r.} = & 1.1513 \log I_{\text{red}} - 2.3026 \log \sigma + 1.1513 \log T \\ & + 52.8356 \end{aligned} \quad (8.30)$$

The vibrational component of the sum over states for diatomic molecules having one degree of freedom of vibration is

$$Z_{\text{vibr}} = \frac{1}{1 - e^{-hc\omega_e/kT}} = \frac{1}{1 - e^{-\theta/T}} \quad (8.31)$$

where ω_e is the frequency of vibration, m^{-1} ; and θ is the characteristic temperature,

$$\theta = (hc/k) \omega_e = 1.4387 \times 10^{-2} \omega_e \quad (8.32)$$

The same component for polyatomic molecules having several degrees of freedom of vibration is

$$Z_{\text{vibr}} = \prod_{i=1}^{3n-6(5)} \frac{1}{1 - e^{-Q_i/T}} \quad (8.33)$$

$$\ln Z = \sum_{i=1}^{3n-6(5)} \ln \frac{1}{1 - e^{-Q_i/T}} \quad (8.34)$$

The electronic component of the sum over states for diatomic molecules is

$$Z_{\text{el}} = g_{0,\text{el}} = 2S + 1 \quad (8.35)$$

where $g_{0,\text{el}}$ is the degeneracy of the zeroth electron level, and S is the total spin of the electrons in the molecule. The term of the molecule's electronic state is determined from Eq. (1.7).

The fraction of the molecules on the energy level with energy ε_i is calculated using Eq. (8.11).

The internal energy is calculated using the equation

$$U - U_0 = \frac{RT^2}{Z} \left(\frac{\partial Z}{\partial T} \right)_V = RT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (8.36)$$

It is more convenient to calculate the internal energy with respect to individual components of the energy of motion:

$$U_{\text{trans}} = 1.5RT \quad (8.37)$$

$$U_{i, \text{rot}} = 0.5RT \quad (8.38)$$

where $U_{i, \text{rot}}$ is the component of the internal energy of rotation for one degree of freedom of rotation.

In the case of diatomic molecules and linear polyatomic ones we are dealing with two degrees of freedom of rotation, while in the case of nonlinear polyatomic molecules we have three such degrees of freedom. The vibrational component of the internal energy

$$\left(\frac{U - U_0}{T} \right)_{\text{vibr}} = \frac{R \frac{\theta}{T}}{e^{\theta/T} - 1} \quad (8.39)$$

The functions $\left(\frac{U - U_0}{T} \right)_{\text{vibr}}$ have been calculated for certain values of θ/T in the case of a linear harmonic oscillator and can be found in tables of Einstein's thermodynamic functions. For polyatomic molecules, the vibrational component of the internal energy is calculated for every degree of freedom of vibration separately and summed over all such degrees of freedom. For linear diatomic and polyatomic molecules the number of vibrational degrees of freedom is

$$f_{\text{vibr}} = 3n - 5 \quad (8.40)$$

and for nonlinear polyatomic molecules it is

$$f_{\text{vibr}} = 3n - 6 \quad (8.41)$$

where n is the number of atoms in the molecule. When the internal rotation has degrees of freedom, in polyatomic molecules we have, for one degree of freedom,

$$U_{i, r.} = 0.5RT \quad (8.42)$$

For gases consisting of diatomic molecules the isochoric heat capacity is determined from the equation

$$C_V = \frac{d(U - U_0)}{dT} = \frac{d}{dT} \left[2.5RT + \frac{RT\theta/T}{e^{\theta/T} - 1} \right] \quad (8.43)$$

It is more convenient to calculate the heat capacity with respect to individual components:

$$C_V = C_{V, \text{trans}} + C_{\text{rot}} + C_{\text{vibr}} \quad (8.44)$$

$$C_{V, \text{trans}} + C_{\text{rot}} = 2.5R \quad (8.45)$$

$$C_{V, \text{vibr}} = \frac{R \left(\frac{\theta}{T} \right)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2} \quad (8.46)$$

In tables of Einstein's thermodynamic functions for a linear harmonic oscillator the function

$$C_E = \frac{R \left(\frac{\theta}{T} \right)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2} \quad (8.47)$$

is given for certain values of θ/T . In the case of polyatomic molecules, the vibrational component of heat capacity equals the sum of C_E over all degrees of freedom of vibration. If a polyatomic molecule has degrees of freedom of internal rotation, one should also take into account $C_{v,i.r.}$ which is the heat capacity associated with internal rotation. According to Eqs. (8.42) and (8.43), we have

$$C_{v,i.r.} = 0.5R \quad (8.48)$$

The entropy of a gas is expressed as the following sum over states*:

$$S_T = R \ln Z + RT \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (8.49)$$

The entropy of a gas consisting of diatomic molecules should be calculated as the sum of the entropies of the following components:

$$S_T = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vibr}} + S_{\text{el}} \quad (8.50)$$

To calculate the translational component of entropy, S_{trans} , one should first calculate $\ln Z$ by Eq. (8.18), while the derivative $\left(\frac{\partial \ln Z}{\partial T} \right)_V$ should be calculated by Eq. (8.19): $\left(\frac{\partial \ln Z}{\partial T} \right)_V = \frac{1.5000}{T}$.

Then

$$S_{T,\text{trans}} = R \ln Z_{\text{trans}} + 1.5000R \quad (8.51)$$

Combination of Eqs. (8.21) and (8.49) gives an expression for calculating the rotational component of entropy:

$$S_{T,\text{rot}} = R \ln Z_{\text{rot}} + R \quad (8.52)$$

The vibrational component of entropy is found in tables of Einstein's thermodynamic functions.

By combining Eqs. (8.35) and (8.49) we derive a formula for calculating the electronic component of entropy:

$$S_{T,\text{el}} = Rg_{0,\text{el}} \quad (8.53)$$

When entropy is calculated by the statistical method for polyatomic molecules, its translational component is similar to that for diatomic molecules. The rotational component of entropy is calculated depending on the molecule type, using Eq. (8.22), (8.23), or (8.24). The vibrational component of entropy for each degree

* Here Z_{trans} is to be calculated according to Eq. (8.15).

of freedom of vibration, θ_i/T , is found in a table of Einstein's thermodynamic functions and summed over all vibrational degrees of freedom. In the case of free internal rotation, the entropy $S_{i.r.}$ is determined from Eq. (8.30) for each degree of freedom of internal rotation, then the components are summed up. The electronic component of entropy is determined from Eq. (8.35).

The function $\frac{A-U_0}{T}$ is calculated using the equation

$$\frac{A_T - U_0}{T} = -R \ln Z \quad (8.54)$$

The function $\frac{A-U_0}{T}$ is calculated as the sum of components corresponding to all types of motion. The function $\left(\frac{A-U_0}{T}\right)_{\text{trans}}$ is calculated using Eq. (8.18) for gases consisting of diatomic and polyatomic molecules. As regards the function $\left(\frac{A-U_0}{T}\right)_{\text{rot}}$ for diatomic gases, it is calculated by Eq. (8.21), and for polyatomic gases it is calculated according to Eq. (8.22), (8.23), or (8.24), depending on the molecule type. The function $\left(\frac{A-U_0}{T}\right)_{\text{vibr}}$ for diatomic molecules is found in tables of Einstein's thermodynamic functions. For polyatomic molecules, the component functions should be summed over all vibrational degrees of freedom. The function $\left(\frac{A-U_0}{T}\right)_{\text{el}}$ is calculated using Eq. (8.35). For polyatomic molecules with degrees of freedom of internal rotation the function $\left(\frac{A-U_0}{T}\right)_{i.r.}$ is determined from Eq. (8.30). Finally, the function $\frac{G-H_0}{T}$ is calculated from the function $\frac{A-U_0}{T}$:

$$\frac{G-H_0}{T} = \frac{A-U_0}{T} + R \quad (8.55)$$

Exercises

1. Determine the translational component of the sum over states for CO at 1.0133×10^5 Pa and 500 K.

Solution. Substitution of the molecular weight, pressure, and temperature into Eq. (8.18) gives

$$\begin{aligned} \ln Z_{\text{trans}} &= 3.4539 \log 28 + 5.7565 \log 500 - 2.3026 \log 1.0133 \\ &\quad \times 10^5 + 8.8612 = 4.9983 + 15.5365 - 11.5262 \\ &\quad + 8.8612 = 17.8669 \\ \log Z_{\text{trans}} &= 7.7607, \quad Z_{\text{trans}} = 5.764 \times 10^7 \end{aligned}$$

2. Determine the rotational component of the sum over states for CO at 500 K. The moment of inertia of CO is $14.49 \times 10^{-47} \text{ kg m}^2$.

Solution. To determine the rotational component of the sum over states use Eq. (8.21). The CO molecule is heteronuclear, hence $\sigma = 1$:

$$\begin{aligned} \ln Z_{\text{rot}} &= 2.3026 \log 14.49 \times 10^{-47} + 2.3026 \log 500 \\ &\quad - 2.3026 \log 1 + 104.5265 \\ &= -105.5487 + 6.2146 + 104.5265 = 5.1924 \\ \log Z_{\text{rot}} &= 2.2550, \quad Z_{\text{rot}} = 179.9 \end{aligned}$$

3. Determine the vibrational component of the sum over states for CO at 500 K if the frequency of vibration is $2.170 \times 10^5 \text{ m}^{-1}$.

Solution. Determine the characteristic temperature from Eq. (8.32):

$$\begin{aligned} \theta &= 1.4387 \times 10^{-2} \times 2.170 \times 10^5 = 3123 \\ \frac{\theta}{T} &= \frac{3123}{500} = 6.245 \end{aligned}$$

To calculate the vibrational component of the sum over states use Eq. (8.31):

$$Z_{\text{vibr}} = \frac{1}{1 - e^{-6.245}} = \frac{1}{1 - 0.00194} = 1.0019$$

4. Determine the sum over states for CO at $1.0133 \times 10^5 \text{ Pa}$ and 500 K.

Solution. The electronic component of the sum over states for CO is $g_{0,\text{el}} = 1$ because the total spin of the electrons is zero. Diatomic molecules have only one vibrational degree of freedom and lack internal rotation. According to Eq. (8.14),

$$Z = 5.764 \times 10^7 \times 179.9 \times 1.0019 = 1.0389 \times 10^{10}$$

5. Determine the fraction of CO molecules on the rotational quantum level $j = 5$ relative to the zeroth vibrational level at 500 K, $Z_{\text{rot}} = 179.9$.

Solution. According to Eq. (8.11),

$$\frac{N_5}{N_A} = 2(5+1) \frac{e^{-B_e 5(5+1)/kT}}{Z_{\text{rot}}}$$

find B_e using Eq. (3.2),

$$B_e = \frac{(6.6256 \times 10^{-34})^2}{8\pi^2 14.49 \times 10^{-47}} = \frac{5.5593 \times 10^{-69}}{14.49 \times 10^{-47}} = 0.3837 \times 10^{-22} \text{ J}$$

$$\frac{N_5}{N_A} = 11 \frac{e^{-30 \times 0.3837 \times 10^{-22} / (1.38054 \times 10^{-23} \times 500)}}{179.9} = 11 \frac{e^{-0.16676}}{179.9} = 0.0518$$

6. Determine the fraction of CO molecules on the vibrational quantum level $v = 1$ and on the zeroth rotational quantum level at 500 K if $Z_{\text{vibr}} = 1.0019$, $\omega_e = 2.170 \times 10^5 \text{ m}^{-1}$, and $\omega_e x_e = 13.37 \times 10^2 \text{ m}^{-1}$.

Solution. To determine the share of CO molecules on the vibrational level use Eq. (8.11). To do this calculate the value of the exponent:

$$\frac{e_{\text{vibr}}}{kT} = \frac{1.5 h c \omega_e - 2.25 h c \omega_e x_e}{1.38054 \times 10^{-23} \times 500} = \frac{64.6537 \times 10^{-21} - 0.5975 \times 10^{-21}}{6.927 \times 10^{-21}} = 9.2473$$

$$\frac{N_1}{N_A} = \frac{e^{-9.2473}}{Z_{\text{vibr}}} = \frac{0.000096}{1.0019} = 0.0000958$$

7. Determine the translational component of internal energy for CO at 500 K.

Solution. The internal energy of translational motion is determined from Eq. (8.37):

$$U_{\text{trans}} = 1.5 \times 8.3143 \times 500 = 6.2357 \times 10^3 \text{ J/mole}$$

8. Determine the rotational component of internal energy for CO at 500 K.

Solution. To determine this component use Eq. (8.38). The CO molecule has two degrees of freedom of rotation:

$$U_{\text{rot}} = 2 \times 0.5 \times 8.3143 \times 500 = 4.1571 \times 10^3 \text{ J/mole}$$

9. Determine the vibrational component of internal energy for CO at 500 K if $\theta/T = 6.245$.

Solution. Find the value of $\left(\frac{U-U_0}{T}\right)_{\text{vibr}}$ in the table of Einstein's thermodynamic functions as a function of θ/T :

θ/T	6.00	6.40
$\left(\frac{U-U_0}{T}\right)_{\text{vibr}}$	0.1243	0.1050

Linear interpolation gives

$$0.40 - 0.0193$$

$$x = 0.0118$$

$$0.245 - x$$

$$\left(\frac{U-U_0}{T}\right)_{\text{vibr}} = 0.1243 - 0.0118 = 0.1125 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$(U-U_0)_{\text{vibr}} = 0.1125 \times 500 = 0.0562 \times 10^3 \text{ J/mole}$$

10. Determine the internal energy of CO at 500 K.

Solution. The electronic component of internal energy is zero, and the molecule lacks degrees of freedom of internal rotation, hence

$$(U - U_0)_{500} = 6.2357 \times 10^3 + 4.1571 \times 10^3 + 0.0562 \times 10^3 \\ = 10.4490 \times 10^3 \text{ J/mole}$$

11. Determine the translational component of heat capacity for CO at 500 K and a constant volume.

Solution. Determine the isochoric translational component of heat capacity for CO using Eq. (8.37):

$$C_{V,\text{trans}} = 1.5 \times 8.3143 = 12.4715 \text{ J mole}^{-1} \text{ K}^{-1}$$

12. Determine the rotational component of heat capacity for CO at 500 K.

Solution. Calculate the rotational component of heat capacity using Eqs. (8.38) and (8.43). The CO molecule has two rotational degrees of freedom, hence

$$C_{\text{rot}} = 2 \times 0.5 \times 8.3143 = 8.3143 \text{ J mole}^{-1} \text{ K}^{-1}$$

13. Determine the vibrational component of heat capacity for CO at 500 K if $\theta/T = 6.245$.

Solution. Find the vibrational component of heat capacity for CO in the table of Einstein's thermodynamic functions for a harmonic oscillator:

θ/T	6.00	6.40
C_E	0.745	0.569

Linear interpolation gives

$$0.40 - 0.176$$

$$0.245 - x \quad x = 0.1078$$

$$C_E = 0.745 - 0.108 = 0.637 \text{ J mole}^{-1} \text{ K}^{-1}$$

14. Determine the heat capacity $C_{P,500}^\circ$ of CO at 1.0133×10^5 Pa and 500 K.

Solution. According to the equation $C_P^\circ = C_V + R$ and Eq. (8.44), we have

$$C_P^\circ = 12.4715 + 8.3143 + 0.637 + 8.3143 = 29.7371 \text{ J mole}^{-1} \text{ K}^{-1}$$

15. Determine the temperature dependence of C_P° . The corresponding equation should be written as $C_P^\circ = a + bT + cT^2$ for temperatures ranging from 298 to 1000 K.

Solution. According to the equation

$$C_P^\circ = 3.5R + C_E = 29.100 + C_E$$

calculate the values of C_P° for the temperatures in the range from 298 to 1000 K at 100 K intervals. Calculate the coefficients a , b , and c by the least squares method.

T, K	$C_P^\circ = y$	$\frac{T-300}{100} = x$	x^2	x^3	x^4	xy	x^2y
298	29.1297	—	—	—	—	—	—
300	29.1295	0	0	0	0	0	0
400	29.3073	1	1	1	1	29.3073	29.3073
500	29.7369	2	4	8	16	59.4738	118.9476
600	30.3511	3	9	27	81	91.0533	273.1599
700	31.0574	4	16	64	256	124.2296	496.9184
800	31.7541	5	25	125	625	158.7705	793.8525
900	32.4170	6	36	216	1296	194.5020	1167.0120
1000	33.0056	7	49	343	2401	231.0392	1617.2744
Σ	246.7589	28	140	784	4676	888.3757	4497.0721

First, find the coefficients X , Y , and Z in the equation of the following type:

$$Y = X + Yx + Zx^2$$

Substitute the corresponding values taken from the table into this equation to derive the following system of equations:

$$246.7589 = 8X + 28Y + 140Z$$

$$888.3757 = 28X + 140Y + 784Z$$

$$4497.0721 = 140X + 784Y + 4676Z$$

Solve the first two equations together:

$$1727.3123 = 56X + 196Y + 980Z$$

$$1776.7514 = 56X + 280Y + 1568Z$$

$$\underline{49.4391 = 84Y + 588Z}$$

Then solve the second two equations together:

$$4441.8785 = 140X + 700Y + 3920Z$$

$$4497.0721 = 140X + 784Y + 4676Z$$

$$\underline{55.1936 = 84Y + 756Z}$$

$$49.4391 = 84Y + 588Z$$

$$55.1936 = 84Y + 756Z$$

$$\underline{5.7545 = 168Z} \quad Z = 0.03425$$

$$Y = \frac{49.4391 - 588 \times 0.03425}{84} = 0.3488$$

$$X = \frac{246.7589 - 140 \times 0.03525 - 28 \times 0.3488}{8} = 29.0247$$

$$C_P^\circ = 29.0247 + 0.3488x + 0.03425x^2 = 29.0247 + 0.3488 \left(\frac{T-300}{100} \right) \\ + 0.03425 \left(\frac{T-300}{100} \right)^2 = 29.0247 + 0.003488T - 3 \times 0.3488 \\ + 0.03425T^2 \times 10^{-4} - 600 \times 10^{-4}T + 9$$

Finally, we derive the following equation for the temperature dependence of interest:

$$C_P^\circ = 28.2866 + 1.433 \times 10^{-2}T + 3.426 \times 10^{-6}T^2$$

16. Determine the internal energy of methanol at 1.0133×10^5 Pa and 500 K.

Solution. The calculation of the translational component of internal energy for polyatomic molecules follows the same pattern as for diatomic molecules. According to Eq. (8.37),

$$U_{\text{trans}} = 1.5RT = 1.5 \times 8.3143 \times 500 = 6.2357 \times 10^3 \text{ J/mole}$$

The molecule of methanol has three rotational degrees of freedom. Consequently, the rotational component of internal energy will be

$$U_{\text{rot}} = 3 \times 0.5RT = 1.5 \times 8.3143 \times 500 = 6.2357 \times 10^3 \text{ J/mole}$$

The methanol molecule also has one degree of freedom of internal rotation. The internal rotation component of internal energy is determined from Eq. (8.42):

$$U_{\text{i.r.}} = 0.5 \times 8.3143 \times 500 = 2.0785 \times 10^3 \text{ J/mole}$$

To determine the vibrational component of internal energy one must sum up 11 terms which are to be found from the experimental values of vibration frequencies and vibration degeneracies, listed in tables of Einstein's thermodynamic functions for a harmonic oscillator:

$\omega_e \times 10^{-5}, \text{ m}^{-1}$	Degeneracy *	$\theta/500$	$\left(\frac{U-U_0}{T} \right),$ J mole ⁻¹ K ⁻¹	$C_E,$ J mole ⁻¹ K ⁻¹
3.683		10.598	0.0025	0.025
2.976	2	8.564	0.0145	0.118
2.845		8.187	0.0193	0.158
1.455	2	4.187	0.537	2.285
1.340		3.856	0.693	2.730
1.116	2	3.211	1.121	3.751
1.031		2.967	1.338	4.186

* Unlike diatomic molecules in which the vibration of atoms is not degenerate, in the case of polyatomic molecules with symmetry several frequencies may coincide in value. Such vibrations are referred to as degenerate:

$$(U-U_0)_{\text{vibr}} = \left(\frac{U-U_{\text{vibr}}}{T} \right) 500 = 6.7281 \times 500 = 3.3640 \times 10^3 \text{ J/mole}$$

In contrast to substances consisting of diatomic molecules, in those consisting of polyatomic ones the vibrational component of internal energy makes an appreciable contribution to the total value of internal energy even at low temperatures:

$$(U - U_0)_{500} = 6.2357 \times 10^3 + 6.2357 \times 10^3 + 2.0785 \times 10^3 \\ + 3.3640 \times 10^3 = 17.9139 \times 10^3 \text{ J/mole}$$

17. Determine the isobaric heat capacity of methanol at 1.0133×10^5 Pa and 500 K.

Solution. Calculate the translational component of heat capacity for polyatomic molecules using Eq. (8.43):

$$C_{V,\text{trans}} = 1.5 \times 8.3143 = 12.4715 \text{ J mole}^{-1} \text{ K}^{-1}$$

The molecule of methanol has three degrees of freedom of rotation, hence the rotational component of heat capacity will be

$$C_{V,\text{rot}} = 1.5 \times 8.3143 = 12.4715 \text{ J mole}^{-1} \text{ K}^{-1}$$

The methanol molecule has one degree of freedom of internal rotation, consequently the internal rotation component of heat capacity will be

$$C_{V,\text{i.r.}} = 0.5 \times 8.3143 = 4.1571 \text{ J mole}^{-1} \text{ K}^{-1}$$

To derive the vibrational component of heat capacity one must sum up 11 terms which are to be found in tables of Einstein's thermodynamic functions for each value of θ/T . The values of θ/T are listed in the table of Problem 16, which also gives the values of C_E for all eleven degrees of freedom of vibration:

$$C_{V,\text{vibr}} = \sum_{i=1}^{11} C_{E_i} = 23.578 \text{ J mole}^{-1} \text{ K}^{-1}$$

The isochoric heat capacity will equal the sum of the components:

$$C_{V,500} = 12.4715 + 12.4715 + 4.1571 + 23.578 \\ = 52.678 \text{ J mole}^{-1} \text{ K}^{-1}$$

The isobaric heat capacity will be

$$C_{P,500}^\circ = 52.678 + 8.314 = 60.992 \text{ J mole}^{-1} \text{ K}^{-1}$$

18. Determine the function $(H^\circ - H_0^\circ)_{500}$ for methanol if $(U - U_0)_{500} = 17.9139 \times 10^3$ J/mole.

Solution. According to Eq. (6.3), for an ideal gas

$$(H^\circ - H_0^\circ)_{500} = 17.9139 \times 10^3 + 8.3143 \times 500 \\ = 22.0711 \times 10^3 \text{ J/mole}$$

19. Determine the entropy of CO at 1.0133×10^5 Pa and 500 K.

Solution. To determine entropy use Eq. (8.49). Equation (8.18) is used to find $\ln Z_{\text{trans}}$, and Eq. (8.19), to determine the derivative

$$\left(\frac{\partial \ln Z_{\text{trans}}}{\partial T} \right)_V. \text{ It equals } 1.5/T. \text{ Then, according to Eq. (8.49),} \\ S_{\text{trans}} = (3.4539 \log 28 + 5.7565 \log 500 - 2.3026 \log 1.0133 \\ \times 10^5 + 8.8612 + 1.5000) 8.3143 = 161.0472 \text{ J mole}^{-1} \text{ K}^{-1}$$

Calculate $\ln Z_{\text{rot}}$ and the derivative $\left(\frac{\partial \ln Z_{\text{rot}}}{\partial T} \right)_V$ using Eq. (8.21). Then,

$$S_{\text{rot}} = (2.3026 \log 14.49 \times 10^{-47} + 2.3026 \log 500 \\ + 104.5265 - 2.3 \log 2 + 1.0000) 8.3143 = 51.4854 \text{ J mole}^{-1} \text{ K}^{-1}$$

The vibrational component of entropy is found as a function of θ/T in the table of Einstein's thermodynamic functions for a harmonic oscillator:

θ/T	6.00	6.40
S_{vibr}	0.146	0.100

Linear interpolation gives

$$0.40 - 0.046 \\ x = 0.028 \\ 0.245 - x$$

Hence, $S_{\text{vibr}} = 0.118 \text{ J mole}^{-1} \text{ K}^{-1}$. The electronic component of entropy of CO is zero because the total spin of the electrons is zero. The entropy of CO equals the sum of the translational, rotational, and vibrational components of entropy:

$$S_{500}^\circ = 161.0472 + 51.4854 + 0.118 = 212.6506 \text{ J mole}^{-1} \text{ K}^{-1}$$

20. Determine the entropy of methanol at 1.0133×10^5 Pa and 500 K.

Solution. To determine the entropy of methanol sum up the translational, rotational, internal rotation, and vibrational components of entropy.

To calculate the translational component of entropy use Eq. (8.49) after having determined $\ln Z_{\text{trans}}$ and found the derivative $\left(\frac{\partial \ln Z_{\text{trans}}}{\partial T}\right)_V$ from Eq. (8.19). Then,

$$S_{\text{trans}} = (3.4539 \log 32 + 5.7565 \log 500 - 2.3026 \log 1.0133 \times 10^5 + 8.8612 + 1.5000) 8.3143 = 162.7142 \text{ J mole}^{-1} \text{ K}^{-1}$$

To calculate the rotational component of entropy use Eqs. (8.25) and (8.49). Calculation of the rotational sum over states calls for determination of the product of the principal moments of inertia. To do the latter, the necessary values should be tabulated. Let the nucleus of the carbon atom be the origin of coordinates. The x axis coincides in direction with the C—O bond. Figure 11 illustrates the

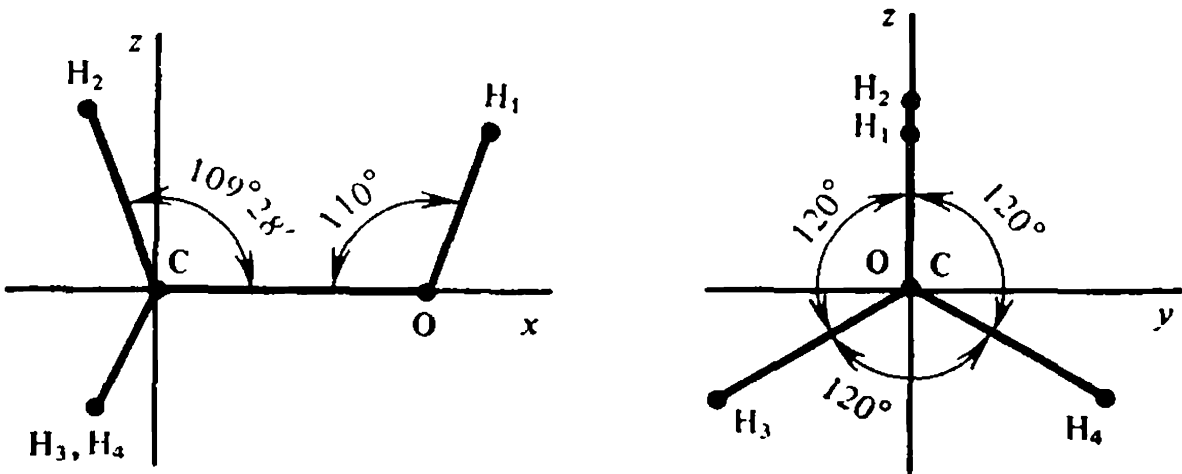


Fig. 11. Projections and geometrical parameters of molecule CH_3OH for calculating the product of moments of inertia

equilibrium internuclear distances and the angles between bonds as well as represents two projections in the xz and yz planes.

Atom	$m \times 10^{26}, \text{ kg}$	$x \times 10^{10}, \text{ m}$	$y \times 10^{10}, \text{ m}$	$z \times 10^{10}, \text{ m}$
C	1.992	0	0	0
O	2.656	1.43	0	0
H ₁	0.166	$1.43 + 0.96 \cos 70^\circ = 1.76$	0	$0.96 \sin 70^\circ = 0.90$
H ₂	0.166	$1.11 \cos 109^\circ 28' = -0.37$	0	$1.11 \sin 70^\circ 32' = 1.05$
H ₃	0.116	-0.37	$1.11 \cos 240^\circ = -0.96$	$1.11 \sin 240^\circ = -0.56$
H ₄	0.166	-0.37	0.96	-0.56

$$\sum_{i=1}^6 m_i = 5.312 \times 10^{-26} \text{ kg}$$

Atom	C	O	H ₁	H ₂	H ₃	H ₄	Σ
$x^2 \times 10^{20}$	0	2.045	3.098	0.137	0.137	0.137	
$y^2 \times 10^{20}$	0	0	0	0	0.922	0.922	
$z^2 \times 10^{20}$	0	0	0.810	1.103	0.314	0.314	
$xy \times 10^{20}$	0	0	0	0	0.355	-0.355	
$xz \times 10^{20}$	0	0	1.584	-0.389	0.207	0.207	
$yz \times 10^{20}$	0	0	0	0	0.538	-0.538	
$mx \times 10^{36}$	0	3.798	0.292	-0.061	-0.061	-0.061	3.907
$my \times 10^{36}$	0	0	0	0	-0.159	0.159	0
$mz \times 10^{36}$	0	0	0.149	0.174	-0.093	-0.093	0.137
$mxy \times 10^{46}$	0	0	0	0	0.059	-0.059	0
$mxz \times 10^{46}$	0	0	0.263	-0.065	0.034	0.034	0.266
$myz \times 10^{46}$	0	0	0	0	0.089	-0.089	0
$m(x^2 + y^2) \times 10^{46}$	0	5.432	0.514	0.023	0.176	0.176	6.321
$m(x^2 + z^2) \times 10^{46}$	0	5.432	0.649	0.206	0.075	0.075	6.437
$m(y^2 + z^2) \times 10^{46}$	0	0	0.134	0.183	0.205	0.205	0.727

Solution of the secular equation (see Chapter 4) gives the following moments of inertia:

$$I_{xx} = 0.727 \times 10^{-46} - \frac{0 + 0.019 \times 10^{-72}}{5.312 \times 10^{-26}} = 0.727 \times 10^{-46} - 0.004 \times 10^{-46} \\ = 0.723 \times 10^{-46}$$

$$I_{yy} = 6.437 \times 10^{-46} - \frac{15.265 \times 10^{-72} + 0.019 \times 10^{-72}}{5.312 \times 10^{-26}} = 6.437 \times 10^{-46} \\ - 2.877 \times 10^{-46} = 3.560 \times 10^{-46}$$

$$I_{zz} = 6.321 \times 10^{-46} - \frac{15.265 \times 10^{-72} + 0}{5.312 \times 10^{-26}} = 6.321 \times 10^{-46} - 2.874 \times 10^{-46} \\ = 3.447 \times 10^{-46}$$

$$I_{xy} = 0 - \frac{0}{5.312 \times 10^{-26}} = 0$$

$$I_{xz} = 0.266 \times 10^{-46} - \frac{0.535 \times 10^{-72}}{5.312 \times 10^{-26}} = 0.266 \times 10^{-46} - 0.101 \times 10^{-46} \\ = 0.165 \times 10^{-46}$$

$$I_{yz} = 0 - \frac{0}{5.312 \times 10^{-26}} = 0$$

The product of the principal moments of inertia will be

$$\begin{aligned}
 I_A I_B I_C &= I_{xx} (I_{yy} I_{zz} - I_{yz} I_{yz}) - I_{xy} (I_{xy} I_{zz} + I_{yz} I_{xz}) \\
 &\quad - I_{xz} (I_{xy} I_{yz} + I_{yy} I_{xz}) \\
 I_A I_B I_C &= 0.723 \times 10^{-46} (3.560 \times 10^{-46} \times 3.447 \times 10^{-46} - 0 \times 0) \\
 &\quad - 0.165 \times 10^{-46} (0 \times 0 + 3.560 \times 10^{-46} \times 0.165 \times 10^{-46}) \\
 &\quad = 0.723 \times 3.560 \times 3.447 \times 10^{-138} \\
 &\quad - 0.165 \times 3.560 \times 0.165 \times 10^{-138} = 8.775 \times 10^{-138}
 \end{aligned}$$

Substitute the product of the principal moments of inertia into Eq. (8.25) to find $\ln Z_{\text{rot}}$ and $\left(\frac{\partial \ln Z_{\text{rot}}}{\partial T}\right)_V$. The CH_3OH molecule is asymmetric. Substitution of the derived values into Eq. (8.49) gives

$$\begin{aligned}
 S_{\text{rot}} &= (1.1513 \log 8.775 \times 10^{-138} + 3.4539 \log 500 \\
 &\quad - 2.3026 \log 1 + 157.3621 + 1.5000) 8.3143 \\
 &= 10.3907 \times 8.3143 = 86.3914 \text{ J mole}^{-1} \text{ K}^{-1}
 \end{aligned}$$

To calculate the internal rotation component of entropy use Eq. (8.30). In the methanol molecule the group of CH_3 atoms rotates relative to the OH group. It may be assumed that the rotation of these groups is free since C—O is a σ -bond. Consequently, the energy of rotation exceeds that of the potential barrier. Find the reduced moment of inertia:

$$\begin{aligned}
 I_{\text{CH}_3} &= 3m_{\text{H}} (r_{\text{C-H}} \sin 70^\circ 32')^2 = 3 \times 0.166 \times 10^{-26} \\
 &\quad \times (1.11 \times 10^{-10} \times 0.943)^2 = 5.454 \times 10^{-47} \text{ kg m}^2 \\
 I_{\text{OH}} &= 1 \times 0.166 \times 10^{-26} (0.96 \times 10^{-10} \sin 70^\circ)^2 = 1 \times 0.166 \\
 &\quad \times 10^{-26} (0.96 \times 0.940 \times 10^{-10})^2 = 1.351 \times 10^{-47} \text{ kg/m}^2 \\
 I_{\text{red}} &= \frac{5.454 \times 10^{-47} \times 1.351 \times 10^{-47}}{5.454 \times 10^{-47} + 1.351 \times 10^{-47}} = 1.083 \times 10^{-47} \text{ kg m}^2
 \end{aligned}$$

The symmetry number equals the product of the degrees of symmetry of the CH_3 and OH groups: $\sigma = 3 \times 1 = 3$. Then,

$$\begin{aligned}
 S_{\text{l.r.}} &= (1.1513 \log 1.083 \times 10^{-47} - 2.3026 \log 3 + 1.1513 \log 500 \\
 &\quad + 52.8356 + 0.5000) 8.3143 = (0.7731 + 0.5000) 8.3143 \\
 &= 1.2731 \times 8.3143 = 10.5849 \text{ J mole}^{-1} \text{ K}^{-1}
 \end{aligned}$$

Determine the vibrational component of entropy as a function of θ/T for all 11 degrees of freedom of vibration. The values of the vibration frequencies, degeneracies, θ/T , and the entropies found

in the table of Einstein's thermodynamic functions for a harmonic oscillator are given below.

$\omega_e \times 10^{-5}, \text{ m}^{-1}$	3.683	2.976	2.845	1.455	1.340	1.116	1.034	1.031
Degeneracy		2		2		2		
θ/T	10.598	8.564	8.187	4.187	3.856	3.211	2.975	2.967
S_{vibr}	0.000	0.015	0.021	0.663	0.872	1.465	1.767	1.779

Then,

$$S_{\text{vibr}} = \sum_{i=1}^{i=11} S_{i,\text{vibr}} = 8.725 \text{ J mole}^{-1} \text{ K}^{-1}$$

Sum up the entropy components to obtain the entropy under the specified conditions:

$$S_{500}^{\circ} = 162.7142 + 86.3914 + 10.5849 + 8.725 \\ = 268.416 \text{ J mole}^{-1} \text{ K}^{-1}$$

The electronic component of entropy is zero because the total spin of the electrons is zero.

21. Determine the function $\left(\frac{G_{500}^{\circ} - H_0^{\circ}}{T}\right)$ for methanol at 500 K and $1.0133 \times 10^5 \text{ Pa}$.

Solution. To determine the above function first calculate the function $\left(\frac{A - U_0}{T}\right)$ according to Eq. (8.54) summing all components over all 18 degrees of freedom of motion:

$$\left(\frac{A - U_0}{T}\right)_{\text{trans}} = -8.3143 (3.4539 \log 32 + 5.7565 \log 500 \\ - 2.3026 \log 1.0133 \times 10^5 + 8.8612) = -8.3143 \times 18.0704 \\ = -150.2427 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\left(\frac{A - U_0}{T}\right)_{\text{rot}} = -8.3143 (1.1513 \log 8.775 \times 10^{-138} + 3.4539 \log 500 \\ - 2.3026 \log 1 + 157.3621) = -8.3144 \times 8.8907 \\ = -73.9199 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\left(\frac{A - U_0}{T}\right)_{\text{i.r.}} = -8.3143 (1.1513 \log 1.083 \times 10^{-47} \\ - 2.3026 \log 3 + 1.1513 \log 500 + 52.8356) = -8.3143 \times 0.7731 \\ = -6.4278 \text{ J mole}^{-1} \text{ K}^{-1}$$

The vibrational component of the function $\frac{A - U_0}{T}$ is found as a function of θ/T for all vibrational degrees of freedom:

$\omega_e \times 10^{-5}, \text{ m}^{-1}$	3.683	2.976	2.845	1.455	1.340	1.116	1.034	1.031
θ/T	10.598	8.564	8.187	4.187	3.856	3.211	2.975	2.967
Degeneracy		2		2		2		
$\left(\frac{A - U_0}{T}\right)_{\text{vibr}}$	0.000	0.000	0.001	0.128	0.179	0.343	0.438	0.441

Then,

$$\left(\frac{A-U_0}{T}\right)_{\text{vibr}} = -2.001 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} \frac{A_{500}-U_0}{T} &= -150.2427 - 73.9199 - 6.4278 - 2.001 \\ &= -232.591 \text{ J mole}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\frac{G_{500}^\circ - H_0^\circ}{T} = -232.591 + 8.3143 = -224.277 \text{ J mole}^{-1} \text{ K}^{-1}$$

22. Determine the function $(H_{500}^\circ - H_{298}^\circ)$ for methanol.

Solution. Use the tabulated value of $(H_{298}^\circ - H_0^\circ)$ from the handbook: $(H_{298}^\circ - H_0^\circ) = 11.435 \text{ kJ/mole}$. Then,

$$\begin{aligned} (H_{500}^\circ - H_{298}^\circ) &= (H_{500}^\circ - H_0^\circ) - (H_{298}^\circ - H_0^\circ) = 22.0711 \times 10^3 \\ &\quad - 11.435 \times 10^3 = 10.636 \times 10^3 \text{ J/mole} \end{aligned}$$

Problems

1. Determine the translational component of the sum over states for F_2 at 298 K and $1.0133 \times 10^5 \text{ Pa}$.

2. Determine the rotational component of the sum over states for F_2 at 298 K. Find the necessary data in the handbook.

3. Determine the vibrational component of the sum over states for F_2 at 298 K. Find the necessary data in the handbook.

4. Determine the electronic component of the sum over states for F_2 . Find the necessary data in the handbook.

5. Determine the sum over states for F_2 at 298 K and $1.0133 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

6. Determine the sum over states for F_2 at 298 K and $0.5 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

7. Determine the sum over states for F_2 at 1000 K and $1.0133 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

8. Determine the sum over states for HI at 1000 K and $1.0133 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

9. Determine the translational component of the sum over states for methane at 1000 K and $1.0133 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

10. Determine the rotational component of the sum over states for methane at 1000 K and $1.0133 \times 10^5 \text{ Pa}$. Find the necessary data in the handbook.

11. Determine the vibrational component of the sum over states for methane at 1000 K if the degeneracies of vibrations are $\nu_s \approx 1$, $\nu_{as} \approx 3$, $\delta_s = 2$, and $\delta_{as} = 3$. Find the necessary vibration frequencies in the handbook.

12. Determine the electronic component of the sum over states for methane at 1000 K.

13*. Determine the sum over states for methane at 1000 K and 1.0133×10^5 Pa. Find the necessary data in the handbook.

14*. Determine the sum over states for CH_3Br at 298 K and 1.0133×10^5 Pa if the internuclear distances are 1.09 Å (C—H) and 1.91 Å (C—Br) and the angles between the bonds are 111° ($\angle\text{HCH}$) and $107^\circ 57'$ ($\angle\text{BrCH}$). The symmetry number is three. The vibration frequencies (cm^{-1}) and degeneracies (in brackets) are 618 (1), 953 (2), 1290 (1), 1453 (2), 2965 (1), and 3082 (2). The degeneracy of the zeroth electron level is unity.

15. Determine the translational component of internal energy for O_2 at 1000 K.

16. Determine the rotational component of internal energy for O_2 at 1000 K.

17. Determine the vibrational component of internal energy for O_2 at 1000 K. Find the necessary data in the handbook.

18. Determine the internal energy ($U - U_0$) and enthalpy ($H^\circ - H_0^\circ$) of O_2 at 1000 K and 1.0133×10^5 Pa. Find the necessary data in the handbook.

19. Determine the internal energy and enthalpy of O_2 at 1000 K and 1.0133×10^5 Pa. Calculate $(H^\circ - H_{298}^\circ)_{1000}$. Find the necessary data in the handbook. Compare the results with the value given in the handbook.

20. Determine the heat capacity C_P° of oxygen at 1.0133×10^5 Pa, and at 298 and 1000 K. Find the necessary data in the handbook. Compare the results with the values given in the handbook.

21. Determine the internal energy and enthalpy of methane at 298 K and 1.0133×10^5 Pa. Find the necessary data in the handbook. Compare the results with the values given in the handbook.

22*. Determine the internal energy and enthalpy of CH_3Br at 298 K and 1.0133×10^5 Pa. The vibration frequencies (cm^{-1}) and degeneracies (in brackets) are 618 (1), 953 (2), 1290 (1), 1453 (2), 2965 (1), and 3082 (2).

23. Determine the translational component of isochoric heat capacity for methane at 1000 K.

24. Determine the rotational component of heat capacity for methane at 1000 K.

25. Determine the vibrational component of heat capacity for methane at 1000 K. Find the wave numbers of vibration in the methane molecule in the handbook. The vibration degeneracies are $\nu_s \approx 1$, $\nu_{as} \approx 3$, $\delta_s \approx 2$, and $\delta_{as} \approx 3$.

26. Determine the heat capacity C_P° of methane at 1000 K if the vibration degeneracies are $\nu_s \approx 1$, $\nu_{as} \approx 3$, $\delta_s \approx 2$, and $\delta_{as} \approx 3$. Find the wave numbers of vibration in the methane molecule in the handbook.

27. Determine the heat capacity C_P° of methane at 298 K. Find the necessary vibration frequencies in the handbook. The vibration

degeneracies are $\nu_s \approx 1$, $\nu_{as} \approx 3$, $\delta_s \approx 2$, and $\delta_{as} \approx 3$. Compare the result with the value given in the handbook.

28*. Determine the heat capacity of CCl_4 in the ideal gaseous state at temperatures ranging from 300 to 1000 K at 100 K intervals. Find the necessary vibration frequencies and degeneracies in the handbook. Derive the temperature dependence of the heat capacity of CCl_4 in the form of the equation $C_P^\circ = a + bT + cT^2$ by the least squares method.

29. Calculate the heat capacity C_P° of water vapour at 1000 K. Find the necessary vibration frequencies in the handbook.

30. Calculate the heat capacity C_P° of carbon dioxide at 1000 K. Find the necessary vibration frequencies in the handbook.

31. Determine the number of methods by which a system of nine different substances can be arranged in three vessels so that the first vessel contains two substances, the second vessel—three substances, and the third—four substances.

32. Calculate the temperature at which the atomic entropy of argon at 1.0133×10^5 Pa is $179.9 \text{ J mole}^{-1} \text{ K}^{-1}$ if the electronic component of the sum over states for argon is unity.

33. Calculate the pressure at which the atomic entropy of atomic iodine at 2000 K is $208.718 \text{ J mole}^{-1} \text{ K}^{-1}$ if the statistical weight of the zeroth electron level is four.

34. Carbon monoxide and nitrogen are diatomic gases with equal molecular weights. Their heat capacities at 298 K and 1.0133×10^5 Pa are 29.15 and $29.10 \text{ J mole}^{-1} \text{ K}^{-1}$, respectively. The internuclear distances are $1.128 \times 10^{-10} \text{ m}$ (C—O) and $1.098 \times 10^{-10} \text{ m}$ (N—N). The entropy of CO is $197.4 \text{ J mole}^{-1} \text{ K}^{-1}$, and that of N_2 is $191.5 \text{ J mole}^{-1} \text{ K}^{-1}$. Explain such a wide discrepancy between the entropy values.

35. CO_2 and SO_2 are triatomic gases. The vibrational component of heat capacity for CO_2 at 300 K is greater than that for SO_2 at the same temperature by $1.47 \text{ J mole}^{-1} \text{ K}^{-1}$. The heat capacities C_P° of these gases at 300 K are 37.13 and $39.87 \text{ J mole}^{-1} \text{ K}^{-1}$, respectively. Draw your conclusions as to the molecular structure of these gases.

36. Calculate the atomic heat capacity C_V , internal energy, and entropy of krypton at 298 K and 1.0133×10^5 Pa. The electronic component of the sum over states for krypton is unity.

37. Calculate the rotational component of entropy for oxygen at 500 K if the internuclear distance is $1.207 \times 10^{-10} \text{ m}$.

38. Calculate the vibrational component of entropy for CO at 298, 1000, and 3000 K if the vibration frequency is $2.170 \times 10^5 \text{ m}^{-1}$.

39. Calculate the entropy of NO at a standard pressure and 298 K if the internuclear distance is $1.15 \times 10^{-10} \text{ m}$ and the vibration frequency is $1.9165 \times 10^5 \text{ m}^{-1}$. The electronic component of the sum over states for NO is four.

40. Calculate the function $\frac{G^\circ - H_0^\circ}{T}$ for Cl_2 at 1.0133×10^5 Pa and 298 K if the internuclear distance is 1.988×10^{-10} m and the vibration frequency is $0.5649 \times 10^5 \text{ m}^{-1}$. The electronic component of the sum over states for Cl_2 is unity.

41. Calculate the function $\frac{G^\circ - H_0^\circ}{T}$ for hydrogen chloride at 298 K and 1.0133×10^5 Pa if the internuclear distance is 1.2715×10^{-10} m and the vibration frequency is $2.9897 \times 10^5 \text{ m}^{-1}$. The electronic component of the sum over states for hydrogen chloride is unity. Also determine $(G_{298}^\circ - H_{298}^\circ)$.

42. Demonstrate that at the absolute zero of temperature, when all particles are at the zeroth energy level, the molar entropy is given by the equation $S_0 = R \ln g_0$, where g_0 is the statistical weight of the zeroth electron level.

43*. Determine the entropy of water vapour in the ideal gaseous state at 298 K and 1.0133×10^5 Pa. Find the molecular constants in the handbook. $\sigma = 2$.

44*. Determine the molar entropy of ethylene at 298 K and standard pressure. Find the molecular constants in the handbook. The electronic component of the sum over states for ethylene is unity.

45. Determine the fraction of NO molecules on the twentieth rotational quantum level at 300 K. Find the molecular constants in the handbook.

46*. Determine the fraction of $^1\text{H}^{35}\text{Cl}$ molecules on the first fifteen rotational quantum levels at 300 K, to within 0.00001. Determine the rotational quantum number of the level on which the number of $^1\text{H}^{35}\text{Cl}$ molecules is maximum under the above conditions. Draw the rotational spectrum at 300 K.

Multivariate Problems

1*. Determine the following parameters of substance A in the ideal gaseous state at temperatures T_1 , T_2 , and T_3 and at a pressure of 1.0133×10^5 Pa: (1) translational, rotational, and vibrational components of the sum over states; (2) sum over states; (3) translational, rotational, and vibrational components of internal energy; (4) internal energy $U - U_0$; (5) translational, rotational, and vibrational components of heat capacity; (6) heat capacity C_P° ; (7) derive the equation $C_P^\circ = f(T)$ in the form of the series $C_P^\circ = a + bT + cT^2$ for temperatures ranging from T_1 to T_3 , using three heat capacity values at the three temperatures; (8) translational, rotational, and vibrational components of entropy; (9) entropy S_T° ; (10) translational, rotational, and vibrational components of the function $\frac{A - U_0}{T}$; (11) function $\frac{A - U_0}{T}$; and (12) function $\frac{G^\circ - H_0^\circ}{T}$. Find the vibra-

tion frequencies and internuclear distances necessary for the calculations in the handbook. Remember that the ground electronic state is $^1\Sigma$.

Variant	Substance A	T_1	T_2	T_3	Variant	Substance A	T_1	T_2	T_3
1	$^{79}\text{Br}^{79}\text{Br}$	300	500	1000	14	$^1\text{H}^{35}\text{Cl}$	300	500	1000
2	$^{79}\text{Br}^{19}\text{F}$	300	600	900	15	$^1\text{H}^{19}\text{F}$	200	400	800
3	$^{12}\text{C}^{16}\text{O}$	200	400	800	16	$^1\text{H}^{127}\text{I}$	300	600	1200
4	$^{13}\text{C}^{16}\text{O}$	300	600	1000	17	$^{14}\text{N}^{14}\text{N}$	200	500	1000
5	$^{35}\text{Cl}^{35}\text{Cl}$	400	800	1000	18	$^{31}\text{P}^{31}\text{P}$	400	600	1200
6	$^{35}\text{Cl}^{19}\text{F}$	300	600	1000	19	$^{127}\text{I}^{127}\text{I}$	400	600	800
7	$^{19}\text{F}^{19}\text{F}$	200	500	1200	20	$^{127}\text{I}^{35}\text{Cl}$	300	500	1000
8	$^2\text{H}^2\text{H}$	200	400	900	21	$^{39}\text{K}^{39}\text{K}$	600	800	1000
9	$^1\text{H}^1\text{H}$	300	600	1000	22	$^{23}\text{Na}^{23}\text{Na}$	600	800	1000
10	$^2\text{H}^3\text{H}$	300	500	900	23	$^7\text{Li}^7\text{Li}$	500	700	900
11	$^3\text{H}^3\text{H}$	400	600	1200	24	$^{11}\text{B}^1\text{H}$	600	800	1000
12	$^1\text{H}^3\text{H}$	300	500	1000	25	$^{11}\text{B}^2\text{H}$	500	700	900
13	$^1\text{H}^{79}\text{Br}$	400	600	1200					

2*. Determine the following parameters of substance A at temperature T and a pressure of 1.0133×10^5 Pa: (1) internal energy $U - U_0$; (2) enthalpy $H^\circ - H_0^\circ$; (3) heat capacity C_P° ; (4) entropy S_T° ; (5) function $\frac{A - U_0}{T}$; and (6) function $\frac{G^\circ - H_0^\circ}{T}$. Find the geometrical parameters of the molecule of substance A, its vibration frequencies and degrees of degeneracy in the handbook.

Variant	Substance A	T	Variant	Substance A	T	Variant	Substance A	T
1	CO_2	300	10	C_2H_2	200	18	H_2O	1000
2	CS_2	400	11	CHCl_3	400	19	H_2S	900
3	N_2O	300	12	CH_3Cl	300	20	SO_2	1000
4	NO_2	250	13	CCl_4	400	21	NH_3	700
5	H_2O	400	14	CO_2	1000	22	PCl_3	1200
6	H_2S	300	15	CS_2	900	23	C_2H_2	1000
7	SO_2	300	16	N_2O	700	24	CHCl_3	1200
8	NH_3	400	17	NO_2	1000	25	H_3Cl	900
9	PCl_3	300						

3. The rotational component of the sum over states for a diatomic homopolar substance is $Z = 50$. Calculate the following for the i th level: (1) ratio of the number of molecules on the i th level to that on the zeroth level, (2) fraction (of the total number) of molecules on the i th level, and (3) fraction of molecules on the zeroth level

Variant	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
j	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

4. Establish the nature of all chemical bonds in the molecules involved in a chemical reaction: (1) determine the geometrical configuration of atoms when the molecules involved in the reaction are in a state of equilibrium; (2) find in the handbook the molecular constants of the substances involved in the reaction; (3) determine the internal energy $U - U_0$ of all the substances involved in the reaction at temperatures ranging from 300 to 1000 K, at 100 K intervals, and also at 298 K; (4) determine the heat capacity C_P° of all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (5) write the equation $C_P^\circ = f(T)$ in the form

$$C_P^\circ = a + bT + cT^2$$

using the results of calculations in Para. 4 by the least squares method for all the substances involved in the reaction; (6) determine the heat of the reaction at 298 K and a constant pressure of 1.0133×10^5 Pa; (7) write the temperature dependence of the heat of the reaction in the form of the equation $\Delta H_T^\circ = A + BT + CT^2 + DT^3$; (8) plot the temperature dependence of the heat of the reaction; (9) determine $(H^\circ - H_0^\circ)$ for all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (10) determine $(H^\circ - H_{298}^\circ)$ at temperatures ranging from 300 to 1000 K, at 100 K intervals; (11) determine the absolute entropies of all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K; (12) determine the functions $\frac{A - U_0}{T}$ for all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (13) determine the functions $\frac{G^\circ - H_0^\circ}{T}$ for all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (14) determine the function $(G^\circ - H_{298}^\circ)$ for all the substances involved in the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (15) determine the changes in entropy during the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; (16) determine ΔG_T° in the course of the reaction at 298 K and at temperatures ranging from 300 to 1000 K, at 100 K intervals; and

(17) find out whether the reaction may proceed spontaneously under standard conditions at temperatures ranging from 298 to 1000 K.

Variant	Reaction	Variant	Reaction
1	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	4	$2\text{CH}_4 + \text{O}_2 \rightleftharpoons 2\text{CO} + 4\text{H}_2$
2	$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2$	5	$2\text{CH}_4 \rightleftharpoons \text{CH} \equiv \text{CH} + 3\text{H}_2$
3	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	6	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$

CHAPTER 9

Gases

Basic Equations and Symbols

The properties of ideal gases are given by the Clapeyron-Mendeleev equation

$$PV = nRT \quad (9.1)$$

in which P is pressure, V is the volume occupied by n moles of the gas, n is the number of moles of the gas, T is absolute temperature, and R is the universal gas constant.

The properties of a mixture of ideal gases are given by the Dalton equation at $T = \text{const}$:

$$P = P_1 + P_2 + P_3 + \dots + P_i = \sum_{i=1}^i P_i \quad (9.2)$$

$$P_i = P x_i \quad (9.3)$$

where P is the total pressure of the gas mixture, P_i is the partial pressure of the i th component, and x_i is the molar fraction of the i th component, as well as by Amagat's equation

$$V = V_1 + V_2 + V_3 + \dots + V_i = \sum_{i=1}^i V_i \quad (9.4)$$

$$V_i = V x_i \quad (9.5)$$

where V is the total volume of the gas mixture, V_i is the partial volume of the i th component, and x_i is the molar fraction of the i th component;

$$x_i = \frac{n_i}{\sum n_i} = \frac{V_i}{V} \quad (9.6)$$

where n_i is the number of moles of the i th component;

$$V_i P = P_i V \quad (9.7)$$

Equations (9.1) through (9.6) apply to real gases at elevated temperatures and low pressures. In calculating the properties of gases it is permissible to apply the laws governing ideal gases to conditions under which the molar volume is at least 5 litres for mono- and diatomic gases and at least 20 litres for more high-molecular gases at 298 K.

The properties of real gases are given by Van der Waals' equation for one mole of gas:

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT \quad (9.8)$$

or for n moles:

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT \quad (9.9)$$

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad (9.10)$$

where a is a constant taking into account the mutual attraction of molecules;

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad (9.11)$$

b is a constant taking into account the intrinsic volume of molecules,

$$b = \frac{2}{3} \pi \sigma^3 N_A \quad (9.12)$$

$$b = \frac{1}{8} \frac{RT_c}{P_c} \quad (9.13)$$

where T_c is the critical gas temperature, P_c is the critical gas pressure, N_A is the Avogadro constant, and σ is the kinetic diameter of gas molecules.

Van der Waals' equation adequately represents the state of a gas if it is at a temperature above critical and one mole of the gas occupies a volume not less than 0.3 litre.

There is another widely used equation representing the properties of real gases, namely

$$Z = PV/nRT \quad (9.14)$$

in which Z is the compressibility factor. For ideal gases $Z = 1$.

Then there is the concept of fugacity f and its coefficient γ_f :

$$f = P^2/P_{1d} \quad (9.15)$$

where P is the pressure of the real gas, and P_{1d} is the pressure that the gas would have at a given volume and temperature if it obeyed

the laws governing ideal gases. Equation (9.12) is applicable only in the case of low pressures. The coefficient γ_f is given by the relation

$$\gamma_f = f/P \quad (9.16)$$

For ideal gases $\gamma_f = 1$. The coefficients z and γ_f for a given temperature and pressure are calculated approximately using a plot (Figs. 12 and 13). Both coefficients are functions of reduced pressure π and reduced temperature τ :

$$\pi = P/P_c, \quad \tau = T/T_c$$

The virial equation of state is

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (9.17)$$

where B and C are the second and third virial coefficients, respectively.

As follows from the molecular-kinetic theory of gases, the temperature dependence of the diameter σ of atoms and molecules is

$$\sigma^2 = \sigma_\infty^2 \left(1 + \frac{C}{T}\right) \quad (9.18)$$

$$\sigma = 2r \quad (9.19)$$

where r is the kinetic radius of atoms and molecules, and σ_∞ and C are constants.

The mean free path length is

$$\lambda = 1/(\sqrt{2} \pi \sigma^2 N) \quad (9.20)$$

where N is the number of molecules per unit volume.

The mean arithmetic velocity of a gas molecule is

$$\bar{u} = \sqrt{8RT/(\pi M)} \quad (9.21)$$

The gas viscosity coefficient is

$$\eta = M/(3\pi\sigma^2 N_A) \quad (9.22)$$

The number of collisions of one molecule per second per unit volume is

$$Z = \sqrt{2} \pi \sigma^2 \bar{u} N \quad (9.23)$$

The number of binary collisions of similar molecules per second per unit volume is

$$Z' = \frac{\sqrt{2}}{2} \pi \sigma^2 N^2 \bar{u} \quad (9.24)$$

where $\pi\sigma^2$ is the cross section of atomic and molecular collisions; the number of collisions between dissimilar molecules per second per unit volume is

$$Z'' = \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \sqrt{8\pi RT \left(\frac{M_1 + M_2}{M_1 M_2}\right)} N_1 N_2 \quad (9.25)$$

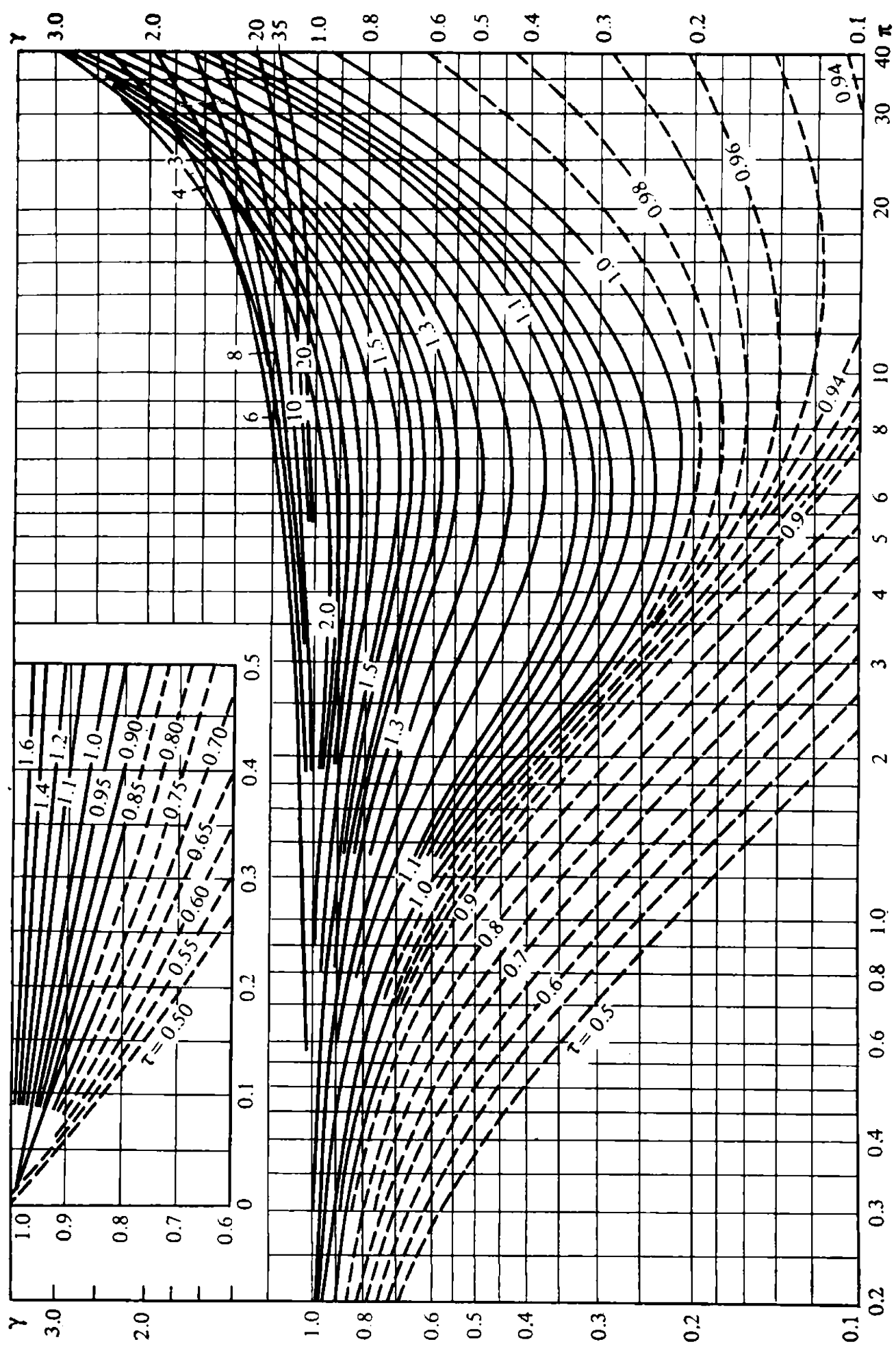


Fig. 12. Activity coefficient (fugacity) of real gases versus reduced pressure and temperature

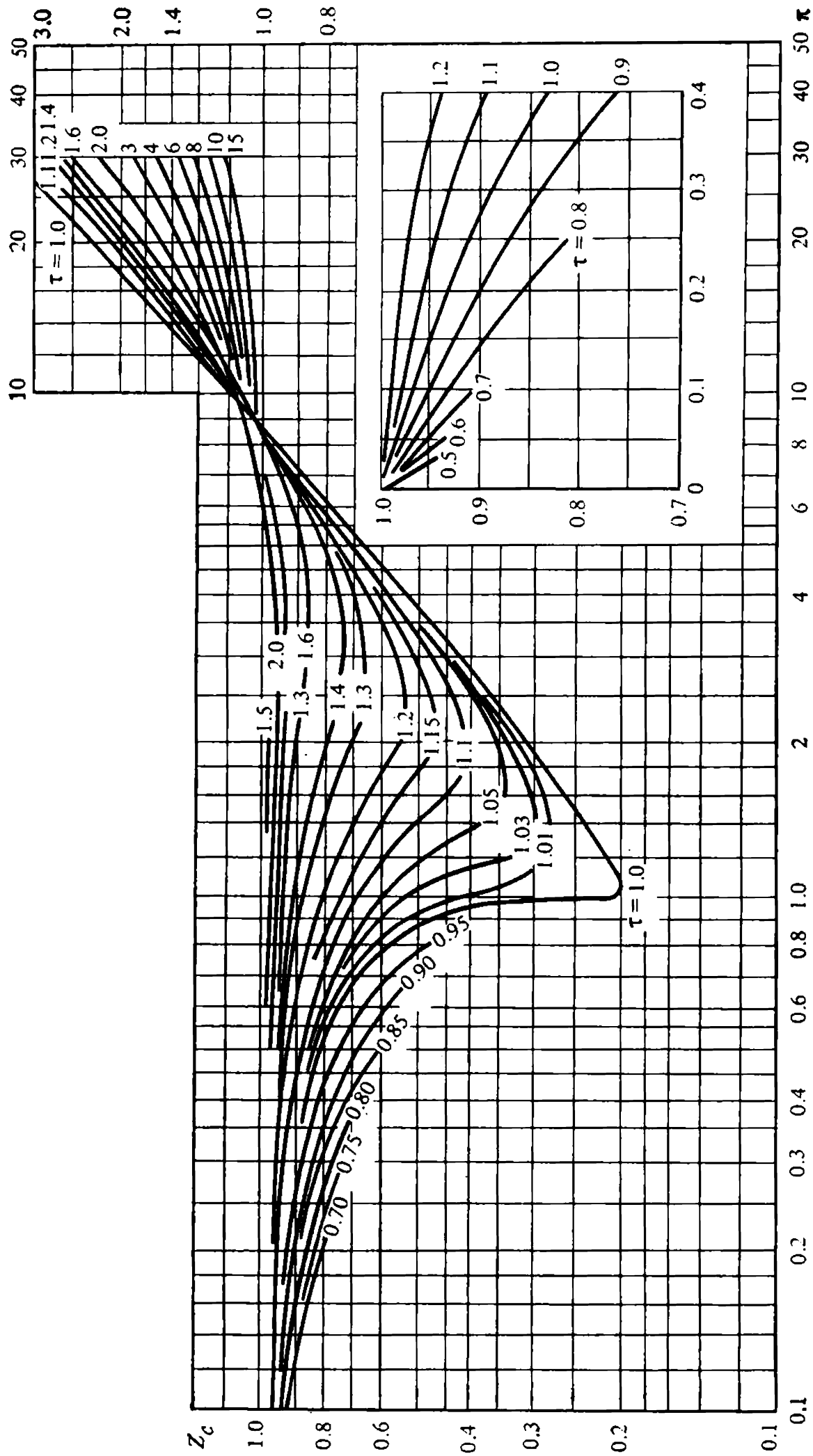


Fig. 13. Compressibility factor z versus reduced pressure π and reduced temperature τ

where N_1 and N_2 stand for the number of molecules of the first and second gases, respectively, within a given volume, M_1 and M_2 are the molecular weights of the first and second gases, σ_1 and σ_2 are the kinetic diameters; the total number of molecular collisions per unit vessel wall surface per second is

$$Z''' = N \sqrt{RT/(2\pi M)} \quad (9.26)$$

The Clapeyron-Mendeleev equation is also applicable to systems in which the gases undergo thermal dissociation. If the number of moles of the gas prior to dissociation is denoted n , the degree of dissociation under a given set of conditions is denoted α , and the number of molecules or atoms into which one molecule of the initial substance dissociates is denoted ν , then in the state of dissociation the number of dissociated moles of the initial substance will be αn , while that of the undissociated moles will be $n + \alpha n = n(1 - \alpha)$. Since every molecule gives ν new molecules as a result of dissociation, dissociation of αn moles of the initial substance yields $\alpha \nu n$ moles of dissociation products. Consequently, the total number of moles in the state of dissociation is

$$n(1 - \alpha) + \alpha \nu n = n(1 - \alpha + \alpha \nu) = n[1 + \alpha(\nu - 1)] \quad (9.27)$$

If we assign the symbol i to the quantity indicating the amount of increase in the number of moles as a result of dissociation, we have the following expression:

$$\begin{aligned} i &= \frac{\text{total number of moles in the state of dissociation}}{\text{number of moles of initial substance before dissociation}} \\ &= \frac{n[1 + \alpha(\nu - 1)]}{n} = 1 + \alpha(\nu - 1) \end{aligned} \quad (9.28)$$

If every molecule of the initial substance dissociates into two new ones ($\nu = 2$), then

$$i = 1 + \alpha \quad (9.29)$$

As can be inferred from expression (9.28), the total number of moles in the state of dissociation equals the original number of moles times i . Hence, Eq. (9.1) as applied to a gas in the state of dissociation takes the form

$$PV = inRT \quad (9.30)$$

Exercises

1. As 0.716 g of an organic substance evaporates at 473 K and 0.999×10^5 Pa, it occupies a volume of 0.246 litre. Calculate the molecular weight of the compound and determine its formula if C : H : O = 2.25 : 0.375 : 1.

Solution. To calculate the molecular weight of the substance use the equation

$$n = PV/(RT) = m/M$$

in which m is the mass of the substance of interest, and M is its molecular weight;

$$M = \frac{8.314 \times 473 \times 0.716}{0.999 \times 10^5 \times 2.426 \times 10^{-4}} = 116.18$$

Having written the formula of the compound in the general form, $C_xH_yO_z$, and knowing its molecular weight and the mass ratio of the constituent elements, write the following three equations

$$z16 + z16 \times 0.375 + z16 \times 2.25 = 116.18 \quad (1)$$

$$y1 = z16 \times 0.375 \quad (2)$$

$$x12 = z16 \times 2.25 \quad (3)$$

(16, 1, and 12 being the atomic masses of O, H, and C, respectively). Solution of the equations gives $z = 2$, $y = 12$, $x = 6$; $C_xH_yO_z = C_6H_{12}O_2$.

2. Reduce a gas to normal conditions (calculate the volume V occupied by a given quantity of gas at 273 K and 1.0133×10^5 Pa) if at 373 K and 1.333×10^3 Pa its volume is $3 \times 10^{-2} \text{ m}^3$.

Solution. Determine the gas volume using Eq. (9.1):

$$\frac{P_1 V_1}{T_1} = \frac{1.0132 \times 10^5 V}{273}$$

$$V = \frac{1.333 \times 10^3 \times 3 \times 10^{-2} \times 273}{373 \times 1.0133 \times 10^5} = 2.89 \times 10^{-4} \text{ m}^3$$

3. Calculate the partial volumes of water vapour, nitrogen, and oxygen as well as the partial pressures of nitrogen and oxygen in moist air. The total volume of the mixture is $2 \times 10^{-3} \text{ m}^3$, its total pressure is 1.0133×10^5 Pa, and the partial pressure of water vapour is 1.233×10^4 Pa. The composition of air by volume is 21% O_2 and 79% N_2 .

Solution. Calculate the partial volume of water vapour, V_{H_2O} , using Eq. (9.5):

$$V_{H_2O} P = V P_{H_2O}$$

$$V_{H_2O} = \frac{2 \times 10^{-3} \times 1.233 \times 10^4}{1.0133 \times 10^5} = 2.4 \times 10^{-4} \text{ m}^3$$

Calculate the partial volumes of O_2 and N_2 :

$$V_{O_2} + V_{H_2O} = V - V_{H_2O} = 0.002 - 0.00024 = 1.76 \times 10^{-3} \text{ m}^3$$

$$V_{O_2}/V_{N_2} = 0.21/0.79$$

Hence,

$$V_{O_2} = 1.76 \times 10^{-3} \times 0.21 = 0.37 \times 10^{-3} \text{ m}^3$$

$$V_{N_2} = 1.76 \times 10^{-3} \times 0.79 = 1.39 \times 10^{-3} \text{ m}^3$$

To calculate the partial pressure of O_2 use Eqs. (9.3) and (9.5):

$$P_{O_2} = P x_{O_2}$$

$$x_{O_2} = V_{O_2}/V = 0.369/2 = 0.184$$

$P_{O_2} = 1.0133 \times 10^5 \times 0.184 = 1.866 \times 10^4 \text{ Pa}$, and since $P = P_{O_2} + P_{N_2} + P_{H_2O}$, then

$$P_{N_2} = 1.0133 \times 10^5 - 1.866 \times 10^4 - 1.233 \times 10^4 = 7.033 \times 10^4 \text{ Pa}$$

4. Calculate the volume occupied by one mole of chlorine at 473 K and $2.0267 \times 10^8 \text{ Pa}$.

Solution. To calculate the volume of Cl_2 use Eq. (9.14). Therefore, find the reduced pressure π and temperature τ with the aid of Eqs. (9.15) and (9.16): $T_c = 417 \text{ K}$; $P_c = 77.09 \times 10^5 \text{ Pa}$; $\tau = 473/417 = 1.13$, $\pi = 2.0267 \times 10^8 / 7.709 \times 10^6 = 26.3$. Calculate the compressibility factor z from Fig. 13: $z = 2.7$;

$$V = 2.7 \times 8.31 \times 473 / (2.027 \times 10^8) = 5.239 \times 10^{-5} \text{ m}^3$$

5. Calculate the pressure of one mole of hydrogen occupying a volume of $0.448 \times 10^{-3} \text{ m}^3$ at 273 K.

Solution. To calculate the pressure use Eq. (9.1):

$$P = 8.31 \times 273 / (0.448 \times 10^{-3}) = 50.633 \times 10^5 \text{ Pa}$$

This result, however, is unreliable because $V \ll 5$ litres. Therefore, repeat the calculation using Eq. (9.10):

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

For hydrogen, $a = 0.244 \text{ litre}^2 \text{ atm/mole}^2$, $b = 0.027 \text{ litre/mole}$;

$$P = \frac{0.082 \times 273}{0.448 - 0.027} - \frac{0.244}{(0.448)^2} = 51.9 \text{ atm } (52.65 \times 10^5 \text{ Pa})$$

6. Calculate the volume of one mole of saturated water vapour at 485 K and $P_{H_2O} = 2.052 \text{ MPa}$ (20.25 atm).

Solution. The calculation is based on selection using Eq. (9.10):

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

For water, $a = 5.464 \text{ litre}^2 \text{ atm/mole}^2$, $b = 0.03 \text{ litre/mole}$. Approximately we assume that

$$V' = \frac{RT}{P} = \frac{0.082 \times 485}{20.25} = 1.964 \text{ litres}$$

Substitute the obtained value into the reduced equation:

$$P' = \frac{0.082 \times 485}{1.96 - 0.03} - \frac{5.464}{1.96^2} = 19.14 \text{ atm}$$

The calculated pressure is below the stated level, hence the true volume is less than 1.964 litre/mole.

Assume that $V'' = 1.75$ litre/mole and repeat the calculation:

$$P'' = \frac{0.082 \times 485}{1.75 - 0.03} - \frac{5.464}{1.75^2} = 21.34 \text{ atm}$$

Consequently, $P'' > P_{\text{H}_2\text{O}}$. Since $P'' > P_{\text{H}_2\text{O}} > P'$, assume that the volume V''' ranges from 1.95 to 1.75 litre/mole and equals 1.85 litre. Then

$$P''' = \frac{0.082 \times 485}{1.85 - 0.03} - \frac{5.464}{1.85^2} = 20.26 \text{ atm}$$

The obtained value differs from the stated one by less than 0.05%, which is why we select the latter result. Hence, $V''' = V = 1.85$ litre/mole ($1.85 \times 10^{-3} \text{ m}^3/\text{mole}$).

7. Calculate the pressure of one mole of ammonia which is in a 100 ml vessel, at 500 K.

Solution. For the above conditions ($V < 0.3$ litre) Eqs. (9.1) and (9.8) are not applicable, therefore, use Eq. (9.17) to calculate the pressure. The virial coefficients for ammonia at 500 K are to be found by way of interpolation from the data listed below:

$T, \text{ K}$	300	400	500	600	800	1000	2000
B	-15.7	0.03	8.53	13.91	20.06	23.33	28.30
C	1115	1000	954	928	894	867	758
B	-4.85	9.31	17.05	21.84	27.26	29.96	33.81
C	1428	1332	1288	1258	1210	1167	1000
B	12.34	14.36	14.98	15.66	16.68	16.72	16.06
C	297	283	271	260	242	227	181
B	—	-332.33	-163.47	-98.83	-47.22	-26.19	1.47
C	—	—	—	4650	2170	1090	319
B	-285	-120.11	-68.30	-45.97	-29.83	-10.19	5.37
C	—	3317	2397	1438	714	461	196
B	-94.03	-49.07	-25	-9.89	7.92	17.70	34.44
C	3116	2499	2173	2005	1852	1786	1622
B	11.12	10.94	10.72	10.51	10.13	9.81	8.72
C	98.29	89.48	82.90	77.63	69.65	63.85	48.09

B is the second virial coefficient, cm^3/mole , and C is the third virial coefficient, $\text{cm}^6/\text{mole}^2$.

$$B = -68.3 \text{ cm}^3/\text{mole}, \quad C = 2397 \text{ cm}^6/\text{mole}^2$$

$$P = \frac{8.31 \times 500 \times 10^{-6}}{0.1 \times 10^{-3}} \left(1 - \frac{68.3}{100} + \frac{2397}{(100)^2} \right) = 14.17 \text{ MPa}$$

8. Calculate the kinetic radius r and the free path length λ for 0.0416 mole of helium occupying a volume of 1 litre at 293 K.

Solution. The kinetic radius of helium atoms is to be calculated using Eq. (9.18). Find the values of σ_∞ and C for helium in the handbook:

$$\sigma_\infty = 1.82 \text{ \AA}, \quad C = 173$$

$$\sigma^2 = 1.82^2 \left(1 + \frac{173}{293} \right) = 5.266 (\text{\AA})^2 (5.266 \times 10^{-20} \text{ m}^2)$$

$$\sigma = 2.295 \text{ \AA}, \quad r = \frac{2.295}{2} = 1.147 \text{ \AA} (1.147 \times 10^{-10} \text{ m})$$

Calculate the free path length λ using Eq. (9.20), but first determine N which is the number of molecules per cubic metre:

$$N = \frac{nN_A}{V} = \frac{0.0416 \times 6.022 \times 10^{23}}{10^{-3}} = 2.506 \times 10^{25} \text{ molecules/m}^3$$

and

$$\lambda = \frac{1}{\sqrt{2} \times 3.14 \times 5.266 \times 10^{-20} \times 2.506 \times 10^{25}} = 1.706 \times 10^{-7} \text{ m}$$

9. Calculate the arithmetic mean velocity \bar{u} of molecules and the viscosity coefficient η for helium under conditions stated in Problem 8.

Solution. To calculate the arithmetic mean velocity use Eq. (9.21):

$$\bar{u} = \left(\frac{8 \times 8.314 \times 293}{3.14 \times 4.003 \times 10^{-3}} \right)^{1/2} = 1244.86 \text{ m/s}$$

Calculate the viscosity coefficient using Eq. (9.22):

$$\eta = \frac{4.003 \times 1244.86 \times 10^2}{3 \times 3.14 \times 5.266 \times 10^{-18} \times 6.022 \times 10^{23}} = 1.668 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1}$$

or 166.8 μP

10. Calculate the number Z of collisions of one helium molecule, the total number Z' of collisions per second per cubic centimetre of volume, and the number Z'' of collisions per square centimetre of the vessel wall surface area per second if 0.146 mole of helium occupies a volume of 1 litre at 293 K.

Solution. To calculate the number Z of collisions of one molecule per second per cubic metre use Eq. (9.23) and the necessary data from the handbook:

$$4r^2 = \sigma^2 = 5.266 \times 10^{-20} \text{ m}^2$$

$$\bar{u} = 1244.86 \text{ m/s}, \quad N = 2.506 \times 10^{25} \text{ molecules/m}^3$$

$$Z = 2 \times 5.266 \times 10^{-20} \times 1244.86 \times 2.506 \times 10^{25} \times 10^{-6} \\ = 2.32 \times 10^{-3}$$

The total number Z' of collisions per second within a volume of 10^{-6} m^3 is to be calculated using Eq. (9.24):

$$Z' = (\sqrt{2}/2) \times 3.14 \times 5.266 \times 10^{-20} (2.506)^2 \times 10^{50} \times 1244.86 \times 10^{-6} \\ = 9.14 \times 10^{28}$$

The number Z''' of collisions against the vessel wall surface within a volume of $1 \times 10^{-4} \text{ m}^3$ is calculated using Eq. (9.26):

$$Z''' = 2.506 \times 10^{25} \left(\frac{8.314 \times 293}{2 \times 3.14 \times 4.003 \times 10^{-3}} \right)^{1/2} 10^{-4} = 7.87 \times 10^{23}$$

11. Determine the number of collisions of nitrogen and argon molecules against one another within a volume of 1 m^3 and the number of their collisions against the vessel wall over an area of 1 m^2 per second at 373 K and at partial pressures of $1.0132 \times 10^5 \text{ Pa}$ (N_2) and $2.0264 \times 10^5 \text{ Pa}$ (Ar) if $\sigma_{\text{N}_2} = 3.64 \text{ \AA}$ and $\sigma_{\text{Ar}} = 3.5 \text{ \AA}$.

Solution. Calculate the mean kinetic radius of the colliding molecules:

$$\bar{\sigma} = \frac{\sigma_{\text{N}_2} + \sigma_{\text{Ar}}}{2} = \frac{3.64 + 3.51}{2} = 3.58 \text{ \AA}$$

To calculate the number of nitrogen and argon molecules per cubic metre use the equation

$$N_i = (P_i V / RT) N_A$$

$$N_{\text{N}_2} = \frac{1.0132 \times 10^5 \times 1 \times 6.022 \times 10^{23}}{8.314 \times 373} = 1.97 \times 10^{25} \text{ molecules/m}^3$$

$$N_{\text{Ar}} = \frac{2.0264 \times 1 \times 6.022 \times 10^{23}}{8.314 \times 373} = 3.934 \times 10^{25} \text{ molecules/m}^3$$

The total number Z'' of collisions per second per cubic metre is calculated using Eq. (9.25):

$$Z'' = N_{\text{N}_2} N_{\text{Ar}} \sigma^2 \left[8\pi RT \left(\frac{M_{\text{Ar}} + M_{\text{N}_2}}{M_{\text{Ar}} M_{\text{N}_2}} \right) \right]^{1/2}$$

$$Z'' = 1.97 \times 10^{25} \times 3.93 \times 10^{25} (3.58 \times 10^{-10})^2 \times 8 \times 3.14 \times 8.314 \times 373 \\ \times \left(\frac{39.94 + 28.01}{39.94 \times 28.01 \times 10^{-3}} \right)^{1/2} = 2.70 \times 10^{35}$$

The number $\sum Z'''$ of collisions of the gas molecules against the vessel wall over an area of 1 m^2 per second is calculated using the equation

$$\sum Z''' = Z'''_{\text{N}_2} + Z'''_{\text{Ar}}$$

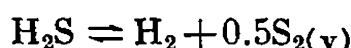
To calculate Z''_{N_2} and Z''_{Ar} use Eq. (9.26):

$$Z''_{N_2} = 1.97 \times 10^{25} \left(\frac{8.314 \times 373}{2 \times 3.14 \times 28 \times 10^{-3}} \right)^{1/2} = 2.61 \times 10^{27}$$

$$Z''_{Ar} = 3.934 \times 10^{25} \left(\frac{8.314 \times 373}{2 \times 3.14 \times 39.9 \times 10^{-3}} \right)^{1/2} = 4.38 \times 10^{27}$$

$$\sum Z''_i = (2.61 + 4.38) 10^{27} = 6.99 \times 10^{27}$$

12. At 945 °C and 1 atm, 1.7 g of H_2S occupy a volume of 5.384 litres. Calculate the degree of dissociation of hydrogen sulphide if the reaction proceeds according to the equation



Solution. Use Eq. (9.30) and assume that $i = 1 + 0.5\alpha$. Then, substitution of the corresponding numerical values into the equation

$$PV = (1 + 0.5\alpha) nRT$$

gives, according to the equation of the reaction,

$$\alpha = \frac{PV}{0.5nRT} - 2 = \frac{1 \times 5.384}{0.5 \times 0.05 \times 0.082 \times 1218} - 2 = 0.156 \text{ or } \alpha = 15.6\%$$

Problems

1. Reduce to normal conditions a gas occupying a volume of $3 \times 10^{-2} \text{ m}^3$ at 373 K and $13.33 \times 10^2 \text{ Pa}$.

2. Determine the molecular weight and write the formula of a substance if the density of its vapour at 373 K and $1.013 \times 10^5 \text{ Pa}$ is 2.55 g/litre. The mass ratio of the constituent elements is C : H = 12 : 1.

3. Determine the amount of carbon dioxide occupying at $5.066 \times 10^5 \text{ Pa}$ and 323 K the same volume that 1 g of helium occupies at $1.013 \times 10^4 \text{ Pa}$ and 273.15 K. What are the densities of these gases?

4. The maximum temperature in a gas-holder is 315 K in summer, and the minimum temperature is 243 K in winter. Calculate the difference (in terms of mass) by which the methane content in the gas-holder having a capacity of 2000 m^3 in winter may exceed that in summer if the pressure is constant and equal to 0.104 MPa (ignore the variations in the gas-holder volume with temperature).

5. A barometer does not read correctly because of the presence of a small amount of air trapped above the mercury column. At a pressure of 755 mm Hg the barometer reads 748 mm Hg, and at 740 mm Hg it reads 736 mm Hg. What is the actual pressure if the barometer reads 750 mm Hg at a constant temperature?

6. Calculate the following parameters of a gas mixture having the composition (% by weight) Cl_2 67, Br_2 28, and O_2 5: (1) composition by volume, (2) partial pressures of the components, and (3) volume of 1 kg of the mixture. The total pressure is 1.013×10^5 Pa. The temperature is 373 K.

7. Oxygen at a pressure of 120 atm has escaped from an oxygen bottle having a capacity of 8 litres into a vessel with a volume of 7.5 m^3 , filled with air at 740 mm Hg and 298 K. Calculate the total pressure in the vessel and the partial volumes of nitrogen and oxygen. (The composition of air is O_2 21% by volume and N_2 79% by volume.)

8. Calculate the amount of CO_2 that can fill a steel vessel having a capacity of $0.5 \times 10^{-3} \text{ m}^3$ at 473 K and 162.1 MPa.

9. Calculate, using Van der Waals' equation, the temperature at which the volume of 1 kg of methane will become equal to 0.1 m^3 at 2.026 MPa.

10. Calculate the b constant in Van der Waals' equation for CO_2 using (a) the critical parameters (handbook) and (2) the kinetic diameter of the CO_2 molecule at 273 K ($\sigma = 3.34 \times 10^{-10} \text{ m}$). Compare the calculated values and explain their being close without complete coincidence.

11. Calculate the volume of 1 kg of methane at 298 K and 3.039 MPa.

12. Up to what temperature can a steel vessel having a capacity of 0.01 m^3 and containing 5 kg of gas A (O_2 , N_2 , H_2 , H_2O , NH_3 , CO_2 , He) be heated if the maximum permissible pressure is 15.2 MPa. Which of the equations of state can be used for the calculation? Estimate the calculation error if Van der Waals' equation is used (with respect to a calculation based on an equation in the virial form). Why do the amounts of error fail to coincide for different gases?

13. At temperature T , one mole of gas A occupies a volume of $0.1 \times 10^{-3} \text{ m}^3$. Calculate the compressibility factor using the virial equation of state and the corresponding states method. Compare the results and determine the error of calculation by the corresponding states method. Calculate the fugacity coefficient γ_f for gas A at T , K, and 10 atm with the aid of Fig. 12.

Variant	1	2	3	4	5	6	7
Gas A	O_2	N_2	H_2	H_2O	NH_3	CO_2	He
T , K	300	300	300	700	500	400	300

14. Calculate the fugacity of ammonia if its molar volume is $3.109 \times 10^{-4} \text{ m}^3/\text{mole}$ at 473 K and 100 atm. Use Eq. (9.12) for approximate calculation. Compare the result with the exact value $f = 82.2 \text{ atm}$. Calculate the fugacity coefficient γ_f .

15. Calculate the arithmetic mean velocity of oxygen molecules at 873 K. At what temperature will helium molecules have the same velocity?

16. At 293 K and 1.013×10^5 Pa, the viscosities of nitrogen and neon are 175 and 311 μP , respectively. Calculate (a) the kinetic diameters of the molecules of these gases and compare the results with the values given in the handbook, and (b) the temperature at which the viscosity of nitrogen becomes equal to that of neon at 293 K.

17. Calculate the mean number of collisions of one molecule, the total number of collisions, and the number of collisions against the vessel wall over an area of 1 m^2 per second for oxygen at pressures of 1.013×10^5 and 1.013 Pa and at a temperature of 323.1 K. The oxygen volume is 0.5 m^3 . Under what conditions (pressure) will the free path length of O_2 molecules become equal to $1 \times 10^{-2} \text{ m}$?

18. Calculate the degree of dissociation of phosgene if 2 g of this gas heated to 500°C occupy a volume of 1.985 litres at a pressure of 1 atm.

19. The degree of dissociation of PCl_5 at 1 atm and 250°C is 80%. Calculate the volume which will be occupied by 1 g of PCl_5 if it is heated to 250°C at 1 atm.

20. At 2500°C and 1 atm, H_2O partially dissociates into H_2 and O_2 . Under these conditions 10 litres of partially dissociated water and that which is at equilibrium with H_2 and O_2 weigh 0.7757 g. Calculate the degree of dissociation of water under the above conditions.

21. At 627°C and 1 atm, SO_3 partially dissociates into SO_2 and O_2 . One litre of the equilibrium mixture weighs 0.94 g under the above conditions. Calculate the partial pressures of the constituent gases in the mixture.

22. The molecular weight of iodine vapour is 241 at 1 atm and 800°C and 212 at the same pressure but at 1027°C . Calculate the degree α of dissociation and the coefficient i for different pressures.

23. The degree of dissociation of N_2O_4 according to the equation $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ at 70°C and atmospheric pressure is 65.6%. Calculate the apparent molecular weight of N_2O_4 under the above conditions.

Multivariant Problems

1. A faulty barometer with air trapped inside reads pressure P_1 , mm Hg, while the true pressure is P_2 , mm Hg. The length of the evacuated portion of the instrument is l , mm, and the temperature is T_1 . Calculate the true pressure if the barometer reads P_3 , mm Hg, at temperature T_2 .

Variant	$P_1, \text{ mm Hg}$	$P_2, \text{ mm Hg}$	$l, \text{ mm}$	$T_1, \text{ K}$	$P_3, \text{ mm Hg}$	$T_2, \text{ K}$	Variant	$P_1, \text{ mm Hg}$	$P_2, \text{ mm Hg}$	$l, \text{ mm}$	$T_1, \text{ K}$	$P_3, \text{ mm Hg}$	$T_2, \text{ K}$
1	745	750	35	283	760	293	14	750	765	30	283	760	273
2	745	765	35	293	750	283	15	740	755	40	273	750	283
3	755	770	25	288	760	298	16	735	755	45	293	740	288
4	730	750	50	298	735	288	17	735	750	45	288	745	293
5	745	760	35	291	755	273	18	735	740	45	298	755	293
6	725	740	55	273	740	291	19	740	766	40	293	745	298
7	725	745	55	283	750	291	20	730	745	50	291	740	273
8	740	745	40	291	745	283	21	725	735	55	273	730	291
9	730	735	50	288	750	291	22	750	755	30	288	755	291
10	725	730	55	291	755	288	23	730	740	50	291	745	282
11	755	760	25	293	770	298	24	745	755	35	293	755	298
12	740	750	40	298	755	283	25	750	760	30	298	765	293
13	735	745	45	283	750	273							

2. Calculate the volume and density of gaseous substance A under conditions close to critical at temperature T and external pressure P . To determine the compressibility factor use the plot of Fig. 13.

Variant	A	T, K	P, MPa	Variant	A	T, K	P, MPa
1	H ₂ O	598	11.75	13	CCl ₄	493	2.23
2	H ₂ O	593	11.0	14	CCl ₄	483	1.5
3	H ₂ O	588	10.3	15	CH ₃ COOH	593	5.6
4	H ₂ O	583	9.6	16	CH ₃ COOH	573	3.2
5	H ₂ O	578	8.95	17	CH ₃ COOH	553	2.5
6	H ₂ O	573	8.36	18	CH ₃ COOH	503	3.8
7	NH ₃	345	3.2	19	CH ₃ COOH	483	3.0
8	NH ₃	335	2.5	20	CH ₃ COOH	463	2.0
9	NH ₃	325	2.0	21	C ₆ H ₆	558	4.3
10	NH ₃	523	1.5	22	C ₆ H ₆	543	3.3
11	CCl ₄	513	2.9	23	C ₆ H ₆	533	2.5
12	CCl ₄	503	2.5	24	C ₆ H ₆	523	2.5

3. g_A , g_B , and g_C kg of gases A, B, and C are mixed in a vessel having capacity V m³ at temperature T . Calculate the partial volumes and pressures of the components and the total pressure of the gaseous mixture (see table on p. 149).

CHAPTER 10

Condensed State of Matter

Basic Equations and Symbols

The polarization of a substance is given by the equation

$$P = P_{or} + P_{at} + P_{el} \quad (10.1)$$

in which P_{or} is orientation polarization, P_{at} is atomic polarization, and P_{el} is electronic polarization;

$$P = P_{or} + P_d = \frac{D-1}{D+2} \frac{M}{d} \quad (10.2)$$

where $P_d = P_{at} + P_{el}$ is polarization by deformation, D is permittivity, M is the molecular weight, and d is the density of the substance;

$$P = \frac{4}{3} \pi N_A (\alpha_{or} + \alpha_{at} + \alpha_{el}) = \frac{4}{3} \pi N_A \alpha \quad (10.3)$$

[illegible]

where N_A is the Avogadro constant, and α is polarizability;

$$\alpha_{\text{or}} = \frac{\mu^2}{3kT} \quad (10.4)$$

where μ is the electric dipole moment, and k is the Boltzmann constant;

$$\frac{D-1}{D+2} \frac{M}{d} = \frac{4}{3} \pi N_A (\alpha_{\text{at}} + \alpha_{\text{el}}) + \frac{4}{9} \frac{\pi N_A}{kT} \mu^2 \quad (10.5)$$

or

$$\mathbf{P} = a + b/T \quad (10.6)$$

where

$$a = \frac{4}{3} \pi N_A (\alpha_{\text{at}} + \alpha_{\text{el}}) \quad (10.7)$$

$$b = \frac{4}{9} \pi N_A \frac{\mu^2}{k} \quad (10.8)$$

$$\mu = \sqrt{\frac{9kb}{4\pi N_A}} \quad (10.9)$$

In the international system of units, the electric dipole moment of nonpolar or weakly polar substances is given by the equation

$$\mu = 4.274 \times 10^{-29} \sqrt{b} \quad (10.10)$$

in which b is a coefficient expressed in $\text{m}^3 \text{K}/\text{mole}$; the off-system unit of the electric dipole moment is debye:

$$\mu = 0.012813 \sqrt{b} \quad (10.11)$$

The molar polarization of a completely ideal solution is

$$\mathbf{P}_{12} = \frac{D_{12}-1}{D_{12}+2} \frac{x_1 M_1 + x_2 M_2}{d_{12}} \quad (10.12)$$

where \mathbf{P}_{12} is the molar polarization of the solution, D_{12} is the solution's permittivity, d_{12} is the solution density, x_1 and x_2 stand for the molar fractions of the solvent and solute, and M is the molecular weight. For a two-component (binary) solution we have

$$\mathbf{P}_{12} = \mathbf{P}_1 x_1 + \mathbf{P}_2 x_2 \quad (10.13)$$

The molar refraction equals the electronic polarization of a substance

$$\frac{n^2-1}{n^2+2} \frac{M}{d} = \frac{4}{3} \pi N_A \alpha_{\text{el}} = R_M \quad (10.14)$$

where R_M is the molar refraction, m^3/mole , d is the density of the substance, kg/m^3 , M is the molecular weight, and n is the refractive index. The specific refraction r equals the molar refraction divided

by the molecular weight:

$$r = \frac{R_M}{M} = \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} \quad (10.15)$$

If a solution contains m_1 kg of a solute in m_2 kg of a solvent, then

$$\left. \begin{aligned} m_1 r_1 &= \frac{n_1^2 - 1}{n_1^2 + 2} \frac{m_1}{d_1}, \quad m_2 r_2 = \frac{n_2^2 - 1}{n_2^2 + 2} \frac{m_2}{d_2} \\ m &= m_1 + m_2 \\ m r &= \frac{n^2 - 1}{n^2 + 2} \frac{m}{d} \end{aligned} \right\} \quad (10.16)$$

Consequently,

$$m r = \frac{n_1^2 - 1}{n_1^2 + 2} \frac{m_1}{d_1} + \frac{n_2^2 - 1}{n_2^2 + 2} \frac{m_2}{d_2} = \frac{n^2 - 1}{n^2 + 2} \frac{m}{d} \quad (10.17)$$

$$R_M = \sum_i n_i R_{at} + \sum_j n_j R_l + \sum_k n_k R_c \quad (10.18)$$

If the atomic polarization is ignored, then

$$\mathbf{P} = R_M + \frac{4}{9} \frac{\pi N_A}{kT} \mu^2 \quad (10.19)$$

Hence, the molecular dipole moment will be

$$\mu = 4.274 \times 10^{-29} \sqrt{(\mathbf{P} - R_M) T} \quad (10.20)$$

For substances in the liquid or solid state,

$$\mu = 4.274 \times 10^{-29} \sqrt{(\mathbf{P} - R_M) T} \quad (10.21)$$

In Eqs. (10.20) and (10.21), polarization and refraction are expressed in m^3/mole . For a narrow range of temperatures which are far from critical the density of a liquid is given by the equation

$$d_T = d_{273} [1 - \alpha (T - 273)] \quad (10.22)$$

in which d_T is the density at temperature T , d_{273} is the density at 273 K, and α is the thermal coefficient of volume expansion;

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (10.23)$$

where V is the volume of the liquid. If it is assumed that $\alpha = \text{const}$ within a narrow temperature range, then

$$\alpha = \Delta V / V \quad (10.24)$$

where ΔV is the change in the volume of the liquid when it is heated by 1° .

The surface tension σ of a liquid corresponds to a change in Gibbs' energy (ΔG) during formation of a unit surface area;

$$\sigma = \Delta G \quad (10.25)$$

$$\sigma = C (d_{\text{liq}} - d_{\text{v}})^4 \quad (10.26)$$

where C is the proportionality factor, d_{liq} is the liquid density, and d_{v} is the vapour density. The temperature dependence of the liquid's surface tension is given by the equation

$$\sigma = \Delta H + T \left(\frac{\partial \sigma}{\partial T} \right)_P \quad (10.27)$$

The viscosity of a liquid is expressed as the intrinsic molecular volume and its specific volume:

$$\eta = C/(v - \omega) \quad (10.28)$$

where η is viscosity, C and ω are constants independent of temperature, and v is the specific volume of the liquid. The temperature dependence of the liquid's viscosity is given by the equation

$$\eta = ke^{E_{\eta}/RT} \quad (10.29)$$

in which E_{η} is the energy of activation of viscous flow.

The heat of evaporation of a liquid for temperatures far from critical is expressed as

$$\Delta H_{\text{evap}, T} = \Delta H_{\text{evap}, 298} + \int_{298}^T \Delta C dT \quad (10.30)$$

where $\Delta H_{\text{evap}, T}$ and $\Delta H_{\text{evap}, 298}$ stand for the heat of evaporation at temperature T and 298 K, and ΔC is the difference between the heat capacities of the vapour and liquid phases.

Calculation of the heat of sublimation of a solid is based on the equation

$$\Delta H_{\text{subl}, T} = \Delta H_{\text{subl}, 298} + \int_{298}^T \Delta C dT \quad (10.31)$$

in which $\Delta H_{\text{subl}, T}$ and $\Delta H_{\text{subl}, 298}$ stand for the heat of sublimation at temperature T and 298 K, and ΔC is the difference between the heat capacities of the vapour and solid phases.

The lattice energy for atomic and molecular crystals can be determined from the equation

$$E = \Delta H_{\text{subl}} \quad (10.32)$$

where E is the lattice energy and ΔH_{subl} is the heat of sublimation; for metals,

$$E = \Delta H_{\text{subl}} + I \quad (10.33)$$

where I is the ionization potential; for ionic crystals,

$$E_{MA} = -\Delta H_{f, MA} + \Delta H_{\text{subl}, M} + \Delta H_{\text{diss}, A_2} + I_M + E_A \quad (10.34)$$

where $\Delta H_{f, MA}$ is the heat of formation of solid substance MA from simple substances, $\Delta H_{\text{subl}, M}$ is the heat of sublimation of the metal, M , I_M is the ionization potential of M , and E_A is the electron affinity of A . According to Kapustinsky's equation,

$$\left. \begin{aligned} E_{MA} &= 1072.24 \times 10^{-7} \frac{z_1 z_2}{r_1 + r_2} \sum_1^i n_i \\ E_{MA} &= 1202.45 \times 10^{-7} \frac{z_1 z_2}{r_1 + r_2} \left(1 - \frac{0.345 \times 10^{-10}}{r_1 + r_2} \right) \sum_1^i n_i \end{aligned} \right\} \quad (10.35)$$

Exercises

1. Determine the polarization of nitrobenzene molecules at 293 K, proceeding from the permittivity and density values.

Solution. Find the permittivity and density of nitrobenzene at 293 K in the handbook: $D_{293} = 35.97$, $d_{293} = 1.2033 \times 10^3 \text{ kg/m}^3$. Use Eq. (10.2) for the calculation:

$$P = \frac{35.97 - 1}{35.97 + 2} \frac{123 \times 10^{-3}}{1.2033 \times 10^3} = 94.143 \times 10^{-6} \text{ m}^3/\text{mole}$$

2. Proceeding from the permittivity of nitrobenzene solutions in benzene and the densities of solutions of several concentrations at 298 K:

$x_{\text{C}_6\text{H}_5\text{NO}_2}$	0.0312	0.0704	0.1028
D	2.98	3.86	4.64
$d \times 10^{-3}, \text{ kg/m}^3$	0.885	0.901	0.914

determine the polarization of nitrobenzene at infinite dilution, P_∞ .

Solution. To determine the polarization P_{12} of the solution use Eq. (10.12):

$$\begin{aligned} x_2 = 0.0312, P_{12} &= \frac{2.98 - 1}{2.98 + 2} \frac{(78 \times 0.9688 + 123 \times 0.0312) 10^{-3}}{0.885 \times 10^3} \\ &= 35.673 \times 10^{-6} \text{ m}^3/\text{mole} \end{aligned}$$

$$\begin{aligned} x_2 = 0.0704, P_{12} &= \frac{3.86 - 1}{3.86 + 2} \frac{(78 \times 0.9294 + 123 \times 0.0704) 10^{-3}}{0.901 \times 10^3} \\ &= 39.614 \times 10^{-6} \text{ m}^3/\text{mole} \end{aligned}$$

$$\begin{aligned} x_2 = 0.1028, P_{12} &= \frac{4.64 - 1}{4.64 + 2} \frac{(78 \times 0.8972 + 123 \times 0.1028) 10^{-3}}{0.914 \times 10^3} \\ &= 45.295 \times 10^{-6} \text{ m}^3/\text{mole} \end{aligned}$$

To determine the polarization of nitrobenzene at each concentration use Eq. (10.13). But first calculate the polarization P_1 of the pure solvent, benzene, with the aid of Eq. (10.2). Find the permittivity of benzene and its density in the handbook:

$$D_{298} = 2.27, \quad d_{298} = 0.874 \times 10^3 \text{ kg/m}^3$$

$$P_1 = \frac{2.27 - 1}{2.27 + 2} \frac{78 \times 10^{-3}}{0.874 \times 10^3} = 26.544 \times 10^{-6} \text{ m}^3/\text{mole}$$

$$x_2 = 0.0312, \quad P_2 = \frac{(35.673 - 26.544 \times 0.9688) 10^{-6}}{0.0312} = 319.140 \times 10^{-6} \text{ m}^3/\text{mole}$$

$$x_2 = 0.0704, \quad P_2 = \frac{(39.614 - 26.544 \times 0.9296) 10^{-6}}{0.0704} = 212.197 \times 10^{-6} \text{ m}^3/\text{mole}$$

$$x_2 = 0.1028, \quad P_2 = \frac{(45.295 - 26.544 \times 0.8972) 10^{-6}}{0.1028} = 208.947 \times 10^{-6} \text{ m}^3/\text{mole}$$

Since each value of P_2 contains an error, use the least squares method to find the relation $P_2 = f(x_2)$ in the form of the equation $P_2 = a + bx_2$.

x_2	$P_2 \times 10^6$	x_2^2	$x_2 P_2 \times 10^6$
0.0312	319.140	0.000973	9.9572
0.0704	212.197	0.004956	14.9387
0.1028	208.947	0.010568	21.4798
$\sum x_2 = 0.2044$	$\sum P_2 = 740.284$ $\times 10^{-6}$	$\sum x_2^2 = 0.016497$	$\sum x_2 P_2 = 46.3757$ $\times 10^{-6}$

The normal equations will take the forms

$$3a + 0.2044b = 740.284 \times 10^{-6}$$

$$0.2044a + 0.016497b = 46.3757 \times 10^{-6}$$

Solution of these equations gives: $a = 354.435 \times 10^{-6}$, $b = -1580.336 \times 10^{-6}$, and the equation for the above relation will take the form

$$P_2 = 354.435 \times 10^{-6} - 1580.336 \times 10^{-6} x_2$$

At $x_2 \rightarrow 0$, $P_2 \rightarrow P_\infty = a$; $P_{2,\infty} = 354.435 \times 10^{-6} \text{ m}^3/\text{mole}$.

3. Determine the polarizability of nitrobenzene at 298 K if the polarization at infinite dilution is $354.435 \times 10^{-6} \text{ m}^3/\text{mole}$.

Solution. To calculate the polarizability use Eq. (10.3):

$$\alpha_2 = \frac{3}{4} \frac{P_{2,\infty}}{\pi N_A} = \frac{3}{4} \frac{354.435 \times 10^{-6}}{\pi 6.02252 \times 10^{23}} = 14.050 \times 10^{-29} \text{ m}^3$$

4. Determine the molar refraction of nitrobenzene at 298 K proceeding from its refractive index and density given in the handbook.

Solution. Find the refractive index and density of nitrobenzene in the handbook: $n = 1.5522$, $d_{298} = 1.2082 \times 10^3 \text{ kg/m}^3$. To calculate the molar refraction use Eq. (10.14):

$$R_M = \frac{1.5522^2 - 1}{1.5522^2 + 2} \frac{123 \times 10^{-3}}{1.1985 \times 10^3} = 32.802 \times 10^{-6} \text{ m}^3/\text{mole}$$

5. Determine the electronic polarizability of nitrobenzene at 298 K if its molar refraction is $32.802 \times 10^{-6} \text{ m}^3/\text{mole}$.

Solution. To calculate the electronic polarizability use Eq. (10.14):

$$\alpha_{el} = \frac{3}{4} \frac{32.802 \times 10^{-6}}{\pi 6.02252 \times 10^{23}} = 1.3003 \times 10^{-29} \text{ m}^3$$

6. Determine the electric dipole moment of the nitrobenzene molecule if the polarization of nitrobenzene at infinite dilution is $354.435 \times 10^{-6} \text{ m}^3/\text{mole}$ and its molar refraction is $32.802 \times 10^{-6} \text{ m}^3/\text{mole}$.

Solution. To calculate the electric dipole moment use Eq. (10.21) assuming that the atomic polarization is small in comparison with P_∞ and R_M :

$$\begin{aligned} \mu &= 4.274 \times 10^{-29} \sqrt{(354.435 \times 10^{-6} - 32.802 \times 10^{-6}) 298} \\ &= 132.099 \times 10^{-31} \text{ C m} \end{aligned}$$

or, in debyes,

$$\mu = 0.01281 \sqrt{(354.435 - 32.802) 298} = 3.96 \text{ D}$$

7. The refractive index and density of propyl ester of chloroacetic acid at 298 K are 1.4035 and $1.090 \times 10^3 \text{ kg/m}^3$, respectively. Determine its molar refraction and compare the result with the value calculated following the additivity rule.

Solution. Use Eq. (10.14) to calculate the molar refraction:

$$R_M = \frac{1.4035^2 - 1}{1.4035^2 + 2} \frac{122.5}{1.090} = 27.455 \text{ m}^3/\text{mole}$$

The value of $(n^2 - 1)/(n^2 + 2)$ can be found in the handbook. To calculate the molar refraction in accordance with the additivity rule (10.18) use the table of atomic refractions:

Atom	Cl	4C	7H	O _{carbonyl}	O _{ester}	ClCOOCH ₂ CH ₂ CH ₃
α , cm ³ /mole	5.967	4×2.418	7×1.100	2.211	1.643	27.193

The molar refraction calculated from the refractive index and density agrees well with the value obtained following the additivity rule.

8. At 293 K the refractive indices and densities of chloroform and chlorobenzene are, respectively: $n_D = 1.4457$, $d = 1488 \text{ kg/m}^3$ and $n_D = 1.5248$, $d = 1110 \text{ kg/m}^3$. Proceeding from the refractive index of a chloroform solution in chlorobenzene and the solution density,

determine the concentration of chloroform: $n_D = 1.4930$, $d = 1260 \text{ kg/cm}^3$.

Solution. Denote the mass concentration of chloroform $x\%$. Then, the concentration of chlorobenzene will be $(100 - x)\%$. Substitute the appropriate values into Eq. (10.17):

$$\frac{1.4930^2 - 1}{1.4930^2 + 2} \frac{100}{1260} = \frac{1.4457^2 - 1}{1.4457^2 + 2} \frac{x}{1488} + \frac{1.5248^2 - 1}{1.5248^2 + 2} \frac{100 - x}{1110}$$

Solution of this equation for x gives $x = 46.8$. Consequently, the concentration of chloroform is 46.8%, and that of chlorobenzene 53.2%.

9. Determine the molar refraction of glycerol $\text{C}_3\text{H}_5(\text{OH})_3$ in water at 293 K if the refractive index of a 10% solution is 1.34481 and its density is $1.0221 \times 10^3 \text{ kg/m}^3$. The refractive index of water is 1.33303, and the water density is $1.0006 \times 10^3 \text{ kg/m}^3$.

Solution. To determine the specific refraction use Eq. (10.17)

$$\begin{aligned} 0.1r_1 &= \frac{1.34481^2 - 1}{1.34481^2 + 2} \frac{1}{1.0221} - \frac{1.33303^2 - 1}{1.33303^2 + 2} \frac{0.9}{1000.6} \\ &= 0.20770 \times 10^{-3} - 0.18503 \times 10^{-3} = 0.02267 \times 10^{-3} \end{aligned}$$

Determine the molar refraction from Eq. (10.15):

$$R_M = \frac{0.02267 \times 10^{-3}}{0.1} 92 \times 10^{-3} = 20.857 \times 10^{-6} \text{ m}^3/\text{mole}$$

10. The temperature dependence of the volume of acetone is given by the following equation:

$$\begin{aligned} V_T &= V_{273} [1 + 1.3240 \times 10^{-3} (T - 273) + 3.8090 \times 10^{-6} \\ &\quad \times (T - 273)^2 - 18.7983 \times 10^{-9} (T - 293)^3] \end{aligned}$$

Its molar volume at 273 K is $71.3846 \text{ cm}^3/\text{mole}$. Determine the coefficient of volume expansion and density of acetone at 315 K.

Solution. To determine the thermal coefficient of volume expansion use Eq. (10.23). To this end, calculate the volume of acetone at 315 K:

$$\begin{aligned} V_{315} &= 71.3846 (1 + 1.3240 \times 10^{-3} \times 42 + 3.8090 \times 10^{-6} \times 42^2 \\ &\quad - 18.7983 \times 10^{-9} \times 42^3) = 75.7344 \text{ cm}^3/\text{mole} \end{aligned}$$

Density is the reciprocal of molar volume, multiplied by the molecular weight:

$$d_{315} = \frac{58 \times 10^{-3}}{75.7344} = 0.7658 \times 10^{-3} \text{ kg/cm}^3$$

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_P &= 71.3846 \times 1.3240 \times 10^{-3} + 2 \times 71.3846 \times 10^{-6} \\ &\quad \times 3.8090 (T - 273) - 3 \times 71.3846 \times 18.7983 \times 10^{-9} (T - 273)^2 = 0.2460 \\ &\quad + 2.7418 \times 10^{-3} T - 4.0257 \times 10^{-6} T^2 \end{aligned}$$

$$\alpha_{315} = 3.2481 \times 10^{-3} + 11.4038 \times 10^{-3} - 5.2744 \times 10^{-3} = 9.3775 \times 10^{-3}$$

11. The densities of liquid benzene at 273 and 304 K are, respectively, 0.9001×10^{-3} and 0.8685×10^{-3} kg/cm³. Determine the density of liquid benzene at 323 K.

Solution. Use Eq. (10.22):

$$\begin{aligned} 0.8685 \times 10^{-3} &= 0.9001 \times 10^{-3} (1 - \alpha 30), \alpha = 1.1702 \times 10^{-3}, \\ d_{323} &= 0.9001 \times 10^{-3} (1 - 1.1702 \times 10^{-3} \times 50) \\ &= 0.8474 \times 10^{-3} \text{ kg/cm}^3 \end{aligned}$$

12. Determine the work of surface formation of one mole of benzene as it forms droplets 0.1 mm in diameter at 293 K.

Solution. First determine the total surface area of one mole of benzene in the form of droplets. Find the density in the handbook: $d_{293} = 0.8790 \times 10^{-3}$ kg/cm³. The volume of one mole is $78/0.8790 = 88.7372$ cm³. The volume of one droplet is

$$V = \frac{4}{3} \pi (0.005)^3 = 0.5236 \times 10^{-6} \text{ cm}^3$$

The area of one droplet is $s = 4\pi (0.005)^2 = 0.314 \times 10^{-3}$ cm². The total surface area of one mole of benzene in the form of droplets is

$$S = \frac{88.7372}{0.5236 \times 10^{-6}} 0.314 \times 10^{-3} = 53.2355 \times 10^3 \text{ cm}^2/\text{mole}$$

Find the surface tension of benzene in the handbook: $\sigma = 28.88 \times 10^{-3}$ N/m. If the surface area of benzene prior to atomization is ignored, then the work of atomization is

$$\Delta G = S\sigma = 28.88 \times 10^{-3} \times 5.3236 = 153.746 \times 10^{-3} \text{ J/mole}$$

13. Determine the surface tension of C₆H₅Br at 323 K.

Solution. Find the value of σ in the handbook: $\sigma = 35.09 \times 10^{-3}$ N/m at 293 K. To calculate the surface tension at the above temperature use Eq. (10.26). The vapour density can be ignored as negligibly low when compared to that of the liquid. Find the density of C₆H₅Br at 293 K in the handbook. Then, Eq. (10.26) will give the coefficient C :

$$C = 35.09 \times 10^{-3} / (1.4948 \times 10^3)^4 = 7.0283 \times 10^{-15}$$

At 323 K, the density of C₆H₅Br is 1.4546×10^3 . Consequently,

$$\sigma_{323} = 7.0283 \times 10^{-15} (1.4546 \times 10^3)^4 = 31.46 \times 10^{-3} \text{ N/m}$$

14. The surface tension of *n*-butanol at 273, 283, and 293 K is 26.2×10^{-3} , 25.4×10^{-3} , and 24.6×10^{-3} N/m, respectively. Determine the change in entropy during formation of 1 m² of surface area of *n*-butanol and the heat of formation at temperatures ranging from 273 to 293 K.

Solution. Use Eq. (10.27). For a narrow temperature range,

$$\left(\frac{\partial \sigma}{\partial T}\right)_P = \frac{\Delta \sigma}{\Delta T}$$

Hence,

$$\Delta H = \sigma - T \frac{\Delta \sigma}{\Delta T} = 25.4 \times 10^{-3} - 283 \frac{24.6 \times 10^{-3} - 26.2 \times 10^{-3}}{293 - 273} = 48.04 \times 10^{-3} \text{ J/m}^2$$

Since $\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \sigma}{\partial T}\right)_P = -\Delta S$

$$\Delta S = -0.08 \times 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}$$

15. Determine the relationship between the viscosity of *n*-propanol and its specific volume. Calculate the viscosity of *n*-propanol at 353 K.

Solution. Use the following transformed form of Eq. (10.28):

$$\frac{1}{\eta} = \frac{V}{C} - \frac{\omega}{C}$$

the general form of this equation being $y = a + bx$, where $a = \omega/C$ and $b = 1/C$. The equation is linear and has the coordinates $1/\eta = f(V)$. The viscosity at several temperatures can be found in the handbook. Find the densities for the same temperatures:

<i>T</i> , K	273	293	313	333
$\eta \times 10^3$, N s m ⁻¹	3.883	2.234	1.400	0.921
$d \times 10^{-3}$, kg/m ³	0.8193	0.8035	0.7875	0.7700

Calculate the fluidities from viscosity and the specific volumes from density. Since each value of viscosity and density contains an error, find the coefficients *a* and *b* by the least squares method:

$v \times 10^3$, m ³ /kg	$1/\eta \times 10^{-3}$, m ² N ⁻¹ s ⁻¹	$v^2 \times 10^6$	$v \frac{1}{\eta}$
<i>x</i>	<i>y</i>	<i>x</i> ²	<i>xy</i>
1.2206	0.2575	1.4899	0.3143
1.2446	0.4476	1.5490	0.5571
1.2698	0.7143	1.6124	0.9070
1.2987	1.0858	1.6866	1.4101
$\sum x = 5.0337 \times 10^{-3}$	$\sum \frac{1}{y} = 2.5052 \times 10^3$	$\sum x^2 = 6.3379 \times 10^{-6}$	$\sum xy = 8.1885$

The normal equations will be

$$\begin{aligned} 4a + 5.0337 \times 10^{-3}b &= 2.5052 \times 10^3 \\ 5.0337 \times 10^{-3}a + 6.3379 \times 10^{-6}b &= 3.1885 \end{aligned}$$

Solution of these equations gives $a = -12.1374 \times 10^3$, $b = 10.1428 \times 10^6$. Hence $C = 9.8592 \times 10^{-8}$, $\omega = +2.1967 \times 10^{-3}$. The equation of interest will be

$$\eta = \frac{9.8592 \times 10^{-8}}{V - 1.1967 \times 10^{-3}}$$

At 353 K, $d = 0.7520 \times 10^3 \text{ kg/m}^3$, consequently, $v = 1.3298 \times 10^{-3} \text{ m}^3/\text{kg}$.

$$\eta = 0.7407 \times 10^{-3} \text{ N s m}^{-2}$$

16. Determine the energy of activation of viscous flow for chlorobenzene. Calculate the viscosity of chlorobenzene at 343 K.

Solution. To determine the energy E_η of activation of viscous flow use Eq. (10.29):

$$\log \eta = \log k + \frac{E_\eta}{2.3026RT} \quad \text{or} \quad y = a + bx$$

where $y = \log \eta$, $a = \log k$, and $b = E_\eta/2.3026RT$. Find the viscosities at several temperatures in the handbook:

$T, \text{ K}$	273	283	293	303	313	323	333
$\eta \times 10^3,$ N s m^2	1.056	0.915	0.802	0.708	0.635	0.573	0.520
$\log \eta$	-2.9763	-3.0386	-3.0958	-3.1500	-3.1972	-3.2418	-3.2840
$(1/T) \times 10^3$	3.663	3.534	3.413	3.300	3.195	3.096	3.003

Since each value of viscosity η contains an error, determine the energy E_η of activation of viscous flow by the least squares method. Write the solution in the form of the following table:

$\frac{1}{T} \times 10^3$	$\log \eta$	$\frac{1}{T^2} \times 10^6$	$\frac{1}{T} \log \eta \times 10^3$
x	y	x^2	xy
3.663	-2.9763	13.418	-10.902
3.534	-3.0386	12.489	-10.738
3.413	-3.0958	11.649	-10.566
3.300	-3.1500	10.890	-10.395
3.195	-3.1972	10.208	-10.215
3.096	-3.2418	9.585	-10.037
3.003	-3.2840	9.018	-9.862
$\sum x = 23.204 \times 10^{-3}$	$\sum y = -21.9837$	$\sum x^2 = 77.257 \times 10^{-6}$	$\sum xy = -72.715 \times 10^{-3}$

$$\begin{aligned}
7a + 23.204 \times 10^{-3}b &= -21.9837 \\
23.204 \times 10^{-3}a + 77.254 \times 10^{-6}b &= -72.715 \times 10^{-3} \\
a + 3.315 \times 10^{-3}b &= 3.1405 \\
b &= 485.714, \quad a = -4.7506 \\
a + 3.329 \times 10^{-3}b &= -3.1337
\end{aligned}$$

The equation of the temperature dependence of viscosity for chlorobenzene will take the form

$$\begin{aligned}
\log \eta &= -4.7506 + 485.714 \times 1/T \\
E_{\eta} &= 485.714 \times 2.3026 \times 8.3143 = 9.2988 \times 10^3 \text{ J/mole}
\end{aligned}$$

The viscosity at 343 K will be

$$\begin{aligned}
\log \eta &= -4.7506 + 485.714 \times 1/343 = -3.3344 \\
\eta &= 0.463 \times 10^{-3} \text{ N s m}^{-2}
\end{aligned}$$

17. Determine the heat of evaporation of one mole of CCl_4 at the normal boiling point, proceeding from the values of $\Delta H_{f,298}$ for liquid and gaseous CCl_4 .

Solution. Find the value of $\Delta H_{f,298}$ in the handbook:

$$\Delta H_{\text{evap},298} = (-106.7 + 139.3) 10^3 = 32.6 \times 10^3 \text{ J/mole}$$

It may be assumed with a high degree of certainty that ΔH does not depend on pressure. Use Eq. (10.30). Since $T_{\text{n.b.}}$ is well below the critical temperature, it may be assumed that ΔC is independent of temperature and equals ΔC_{298} :

$$\Delta H_{T_{\text{n.b.}}} = \Delta H_{298} + \int_{298}^{T_{\text{n.b.}}} \Delta C dT$$

Find the normal boiling point in the handbook: $T_{\text{n.b.}} = 349.7 \text{ K}$:

$$\Delta H_{T_{\text{n.b.}}} = 32.6 \times 10^3 + (83.4 - 131.7) (349.7 - 298) = 30.1 \times 10^3 \text{ J/mole}$$

18. The heats of formation of LiI at 298 K in the gaseous and solid states are -67.0 and -271.3 kJ/mole , respectively. The temperature dependence of the heat capacity of solid LiI is given by the equation

$$C_P^\circ = 51.50 + 10.22 \times 10^{-3}T$$

The heat capacity of gaseous LiI is

$$C_P^\circ = 36.68 + 14.24 \times 10^{-3}T$$

Determine the heat of sublimation of LiI at 680 K.

Solution. To determine the heat of sublimation use Eq. (10.31):

$$\begin{aligned}\Delta H_{680} = & (-67.0 \times 10^3 + 271.3 \times 10^3) + \int_{298}^{680} [(36.68 - 51.50) \\ & + (14.24 - 10.22) 10^{-3} T] dT = 204.3 \times 10^3 - 14.82 (680 - 298) \\ & + \frac{4.02 \times 10^{-3}}{2} (680^2 - 298^2) = 199.39 \times 10^3 \text{ J/mole}\end{aligned}$$

19. Calculate the ionic lattice energy of magnesium chloride, proceeding from the thermodynamic cycle and Kapustinsky's equations. Compare the results with the values given in the handbook.

Solution. Find the values necessary for the calculation in the handbook: $\Delta H_{f,298,\text{MgCl}_2}^\circ = -641.83 \text{ kJ/mole}$, $\Delta H_{\text{subl,Mg}} = 1505.5 \text{ kJ/mole}$, $\Delta H_{f,298,\text{Cl}}^\circ = 121.3 \text{ kJ/mole}$, $I_{\text{Mg}} = 2187 \text{ kJ/mole}$ (ionization potential), and $E = -363 \text{ kJ/mole}$ (electron affinity of Cl).

$$\begin{aligned}E_{\text{MgCl}_2} &= (641.83 + 150.5 + 242.6 + 2187.0 - 726.0) 10^3 \\ &= 2495.9 \times 10^3 \text{ J/mole}\end{aligned}$$

Calculate the ionic lattice energy using Eq. (10.35). To do this substitute into Eq. (10.35) the ionic charges $z_1 = 2$, $z_2 = 1$, as well as $\Sigma n = 3$, $r_{\text{Mg}^{2+}} = 0.74 \times 10^{-10} \text{ m}$, and $r_{\text{Cl}^-} = 1.81 \times 10^{-10} \text{ m}$. Then,

$$E_{\text{MgCl}_2} = 1072.2 \times 10^{-7} \frac{2 \times 1}{(0.74 + 1.81) 10^{-10}} 3 = 2520 \times 10^3 \text{ J/mole}$$

or

$$\begin{aligned}E_{\text{MgCl}_2} &= 1202.5 \times 10^{-7} \frac{2 \times 1}{(0.74 + 1.81) 10^{-10}} \left[1 - \frac{0.345 \times 10^{-10}}{(0.74 + 1.81) 10^{-10}} \right] \\ &= 2450 \times 10^3 \text{ J/mole}\end{aligned}$$

According to the handbook, $E_{\text{MgCl}_2} = 2493 \times 10^3 \text{ J/mole}$.

Problems

1. Determine the polarization of chloroform at 293 K, using the permittivity and density values given in the handbook.

2. Given the permittivity of aniline solutions in dioxane and the densities of the solutions at 298 K, determine the polarization of aniline at infinite dilution:

$x_{\text{C}_6\text{H}_5\text{NH}_2} \times 10^3, \text{ mol. frac.}$	0	9.77	35.67
D	2.6037	2.2508	2.3744
$d, \text{ g/cm}^3$	1.0280	1.0279	1.0276

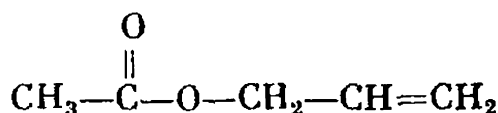
3. Proceeding from the polarization of chloroform at infinite dilution, its refractive index and density at 293 K according to the handbook, determine the dipole moment of CHCl_3 .

4*. Proceeding from the polarization of acetone at infinite dilution in a nonpolar solvent at several temperatures according to the handbook, determine the electric dipole moment of the acetone molecule.

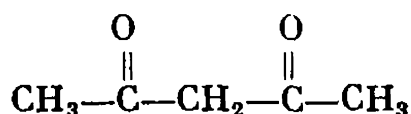
5. The refractive index and density of propyl ester of chloroacetic acid at 293 K are 1.4035 and 1090 kg/m³, respectively. Determine its molar refraction and compare the result with the value obtained following the additivity rule.

6. Determine the molar refraction of pyrrole C₄H₅N if its refractive index is 1.5034 and density 929 kg/m³. Compare the result with the value obtained following the additivity rule.

7. Which of the two structures



or



is identified with the compound having the empirical formula C₅H₈O₂ if its refractive index at 298 K is 1.4045 and its density is 928 kg/m³.

8. Given the permittivity and density of benzene at 283, 293, 303, and 313 K, determine its molar polarization and electric dipole moment.

9. Determine the volume to be occupied by 1500 kg of amyl alcohol (1-pentanol) at 390 K. Find its density and thermal coefficient of volume expansion in the handbook.

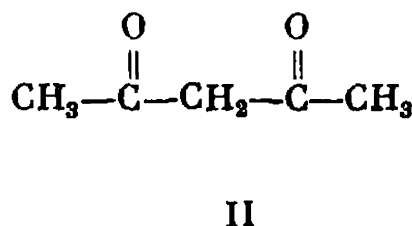
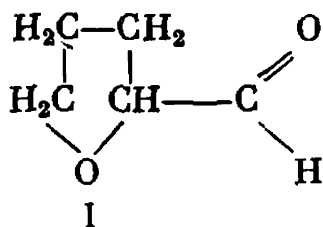
10. The temperature dependence of the volume of diethyl ester of oxalic acid in the range of 273 to 414 K is given by the equation

$$V_T = V_{273} [1 + 1.06031 \times 10^{-3} (T - 273) + 1.0983 \times 10^{-6} \times (T - 273)^2 + 2.6657 \times 10^{-9} (T - 273)^3]$$

Determine the density of diethyl ester of oxalic acid at 443 K if its density at 293 K is 1.0785 × 10³ kg/m³.

11. Given the surface tension and density of CCl₄ at 273, 283, 293, 303, 313, 323, and 333 K, prove that the quantity $\sigma^{1/4}M/d$ is independent of temperature. Calculate this quantity.

12. The following are among the possible structures of the compound having the empirical formula C₅H₈O₂:



Establish the structure of the compound if its surface tension at 298 K is 0.0433 N/m and density $1.1094 \times 10^3 \text{ kg/m}^3$, using the appended table of parachor increments.

13. The empirical formula of a compound is $\text{C}_4\text{H}_5\text{N}$. Define its structural formula if the density of the compound is 969 kg/m^3 at 293 K and its surface tension at the same temperature is $37.52 \times 10^{-3} \text{ N/m}$.

14*. Derive the equation for the temperature dependence of surface tension using the values of the latter at several temperatures according to the handbook. Let the equation be of the $\sigma = a + bT$ type. Use the least squares method.

15. Determine the change in entropy during formation of 1 m^2 of surface area of liquid chlorobenzene, using the handbook.

16. Determine the change in enthalpy during formation of 1 m^2 of surface area of liquid chlorobenzene at 293 K. Find the necessary values in the handbook.

17*. Derive the equation for the fluidity $1/\eta$ of nitrobenzene as a function of specific volume, using the least squares method and the necessary data from the handbook. Determine the viscosity of nitrobenzene at 373 K if its density at the same temperature is $1.1245 \times 10^3 \text{ kg/m}^3$.

18*. Determine the energy of activation of viscous flow for benzene, proceeding from the viscosity at several temperatures according to the handbook. Derive the equation for the temperature dependence of the viscosity of benzene using the least squares method.

19. Determine the heat of evaporation of sulphuryl chloride SO_2Cl_2 at the normal boiling point. Find the necessary data in the handbook.

20. Derive the equation for the temperature dependence of the heat of evaporation of TiCl_4 , applicable within the temperature range from 298 to 400 K. Ignore the dependence of ΔH on pressure. Find the necessary data in the handbook.

21. The heat of formation of naphthalene in the solid and ideal gaseous states at 298 K is, respectively, 78.073 and 150.959 kJ/mole. The heat capacities C_P° of solid and gaseous naphthalene at 298 K are 693.289 and 132.549 J mole $^{-1}$ K $^{-1}$, respectively. Determine the heat of sublimation of naphthalene at 340 K and the change in entropy at the same temperature.

22. Proceeding from the data given in the handbook, determine the lattice energy of I_2 at 298 K.

23. Determine the lattice energy of diphenyl $\text{C}_{12}\text{H}_{10}$ at 298 K if the heat of its formation in the gaseous state is 182.09 kJ/mole. The other necessary data can be found in the handbook.

24. Determine the lattice energy of potassium at 298 K. Find the necessary data in the handbooks.

25. Determine the lattice energy of KBr at 298 K, $\Delta H_{\text{subl,K}} = 89.998 \text{ kJ/mole}$. Find the necessary data in the handbook.

Multivariant Problems

1. Calculate the electric dipole moment of substance A proceeding from the polarization at infinite dilution in a nonpolar solvent at several temperatures according to the handbook. Calculate the molar refraction, proceeding from the density and refractive index at a particular temperature, and determine approximately the electric dipole moment from the polarization at infinite dilution and molar refraction at a particular temperature.

Variant	Substance A	Variant	Substance A	Variant	Substance A
1	CHCl ₃	10	CH ₃ OCH ₃	18	C ₂ H ₅ OC ₂ H ₅
2	C ₂ H ₅ OH	11	C ₂ H ₅ OC ₂ H ₅	19	C ₆ H ₅ Br
3	CH ₃ COCH ₃	12	C ₆ H ₅ Br	20	C ₆ H ₅ Cl
4	C ₂ H ₅ OC ₂ H ₅	13	C ₆ H ₅ Cl	21	C ₆ H ₅ NO ₂
5	C ₆ H ₅ Br	14	C ₆ H ₅ NO ₂	22	CHCl ₃
6	C ₆ H ₅ Cl	15	CHCl ₃	23	C ₂ H ₅ OH
7	C ₆ H ₅ NO ₂	16	C ₂ H ₅ OH	24	CH ₃ COCH ₃
8	CHCl ₃	17	CH ₃ COCH ₃	25	C ₂ H ₅ OC ₂ H ₅
9	C ₂ H ₅ OH				

2. At 293 K, the density of an $a\%$ solution of substance A in solvent B is d , and the refractive index of the solution is n . Calculate the molar refraction of substance A if the density of solvent B at 293 K is d_0 and its refractive index at the same temperature is n_0 .

Variant	$a, \%$	A	B	$d \times 10^{-3}, \text{ kg/m}^3$	n
1	20	HCl	CH ₃ OH	0.915	1.374
2	31	HCl	H ₂ O	1.157	1.407
3	30	H ₂ SO ₄	H ₂ O	1.220	1.370
4	40	HClO ₃	H ₂ O	1.293	1.367
5	17	LiBr	H ₂ O	1.129	1.362
6	35	LiCl	H ₂ O	1.174	1.414
7	24.5	NaCl	H ₂ O	1.187	1.377
8	12.5	Na ₂ SO ₄	H ₂ O	1.116	1.352
9	9	K ₂ SO ₄	H ₂ O	1.075	1.345
10	50	SnCl ₄	CH ₃ COOC ₂ H ₅	1.487	1.476
11	44	CO(NH ₂) ₂	H ₂ O	1.121	1.400
12	90	C ₂ H ₄ Br ₂	C ₃ H ₇ OH	1.866	1.503

Variant	α , %	A	B	$d \times 10^{-3}$, kg/m ³	n
13	22	CCl ₃ COOLi	H ₂ O	1.128	1.365
14	29	CH ₃ COOH	H ₂ O	1.038	1.353
15	50	CH ₃ COOH	C ₆ H ₆	0.947	1.434
16	50	CH ₃ COCH ₃	C ₆ H ₆	0.839	1.428
17	45	CCl ₃ COOH	H ₂ O	1.255	1.395
18	42	CCl ₃ COONa	H ₂ O	1.295	1.397
19	52	SCNC ₃ H ₅	C ₅ H ₁₀ NH	1.075	1.580
20	25	SCNC ₃ H ₅	<i>o</i> -C ₆ H ₄ (CH ₃) ₂	0.968	1.551
21	40	C ₅ H ₁₀ NH	SCNC ₃ H ₅	1.085	1.582
22	37	C ₆ H ₅ SO ₃ H	H ₂ O	1.135	1.406
23	66	C ₆ H ₅ NH ₂	C ₂ H ₅ OH	0.959	1.516
24	3.6	C ₆ H ₅ COOH	C ₆ H ₅ CH ₃	0.856	1.493
25	44	C ₁₂ H ₂₂ O ₁₁	H ₂ O	1.191	1.406

The refractive index and density of solvent B are as follows:

Solvent B	$d_0 \times 10^{-3}$, kg/m ³	n_0	Solvent B	$d_0 \times 10^{-3}$, kg/m ³	n_0
H ₂ O	1.000	1.333	SCNC ₃ H ₅	1.019	1.530
CH ₃ OH	0.805	1.329	C ₅ H ₁₀ NH	0.863	1.461
C ₂ H ₅ OH	0.808	1.364	C ₆ H ₆	0.885	1.504
CH ₃ COOC ₂ H ₅	0.903	1.375	C ₆ H ₅ CH ₃	0.867	1.497
CH ₃ CH ₂ CH ₂ OH	0.807	1.386	<i>o</i> -C ₆ H ₄ (CH ₃) ₂	0.881	1.505

3. Calculate the parachor of substance A proceeding from known surface tension and density at temperature T . Compare the result with the value obtained following the additivity rule. See the appendix or handbook.

Variant	Substance A	$\sigma \times 10^3$, N/m	$d \times 10^{-3}$, kg/m ³	T , K
1	CHCl ₃	27.28	1.489	293
2	CH ₃ CHO	21.2	0.783	293
3	ClCH ₂ CH ₂ OH	42.2	1.213	293
4	CH ₃ CH ₂ OH	22.75	0.789	293
5	CH ₃ COCH ₃	23.7	0.791	293
6	CH ₃ COOCH ₃	24.6	0.924	293

Variant	Substance A	$\sigma \times 10^3$, N/m	$d \times 10^{-3}$, kg/m ³	T, K
7	CH ₃ CH ₂ CH ₂ OH	23.78	0.804	293
8	CH ₃ COOC ₂ H ₅	23.9	0.901	293
9	C ₂ H ₅ OC ₂ H ₅	16.6	0.708	298
10	CH ₃ COC ₂ H ₅	24.6	0.810	293
11	C ₆ H ₆	28.89	0.879	293
12	<i>n</i> -C ₆ H ₁₄	18.43	0.659	293
13	<i>n</i> -C ₅ H ₁₁ OH	21.6	0.815	293
14	C ₆ H ₅ Br	36.34	1.508	283
15	C ₆ H ₅ Cl	33.2	1.107	293
16	C ₆ H ₅ NH ₂	42.9	1.022	293
17	C ₇ H ₅ CH ₃	39.8	0.885	273
18	CH ₃ COC ₆ H ₅	38.7	1.033	288
19	C ₆ H ₅ CH ₂ CH ₃	29.2	0.867	293
20	C ₉ H ₇ N	45.0	1.095	293
21	CH ₂ OHCH ₂ OH	46.1	1.109	293
22	CH ₂ (CH ₂) ₄ CH ₂	24.95	0.779	293
23	C ₆ H ₅ CH(CH ₃) ₂	28.20	0.862	293
24	(CH ₃) ₃ C—CH(CH ₃)(CH ₂) ₂ CH ₃	31.27	0.894	293
25	C ₆ H ₅ COOCCH ₃	37.3	1.088	293

CHAPTER 11

Phase Equilibrium of One-Component Systems

Basic Equations and Symbols

The phase equilibrium conditions are given by the following formulas:

$$\mu_i^\alpha = \mu_i^\beta \quad (11.1)$$

$$f_i^\alpha = f_i^\beta \quad (11.2)$$

in which μ_i^α and μ_i^β are the chemical potentials of the i th component in phases α and β which are at equilibrium, while f_i^α and f_i^β are fugacities.

In a heterogeneous system, the relationship between the number of degrees of freedom, the number of phases, and the number of components is expressed in terms of Gibbs' phase rule

$$f = C - Ph + 2 \quad (11.3)$$

where C is the number of components ($C = R - q$, R being the number of substances and q being the number of independent reac-

tions), Ph is the number of phases, and f is the variance of the system (the number of thermodynamic degrees of freedom).

The relationship between the basic thermodynamic parameters of a one-component two-phase system in the state of equilibrium is given by the Clapeyron-Clausius equation. The differential forms of this equation are

$$\frac{dP}{dT} = \frac{\Delta H_{p.c.}}{T\Delta V_m}, \quad \Delta H_{p.c.} = T \frac{dP}{dT} \Delta V_m \quad (11.4)$$

where $\Delta H_{p.c.}$ is the heat of phase change under conditions of phase equilibrium (evaporation, fusion, sublimation, transformation of modifications), dP/dT is the temperature coefficient of saturated vapour pressure, and ΔV_m is the difference between the molar volumes of the phases at equilibrium.

For equilibria solid \rightleftharpoons vapour and liquid \rightleftharpoons vapour in the range of temperatures far from critical, provided that $V_v = RT/P$,

$$\frac{d \ln P}{dT} = \frac{\Delta H_{p.c.}}{RT^2} \quad (11.5)$$

Integration of Eq. (11.5) with $\Delta H_{p.c.} = \text{const}$ gives

$$\log P = -\frac{\Delta H_{p.c.}}{2.3RT} + \text{const} \quad (11.6)$$

$$\log P = A - B/T \quad (11.7)$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{p.c.}}{2.3R} \frac{T_2 - T_1}{T_2 T_1} \quad (11.8)$$

In Eqs. (11.5) and (11.7), $\Delta H_{p.c.}$ is a mean value applicable to the temperature range T_1 - T_2 .

Trouton's equation (for nonpolar substances) is

$$\frac{\Delta H_{\text{evap}}}{T_{n.b.}} = 21 \quad (11.9)$$

where $T_{n.b.}$ is the normal boiling point at a pressure of 1.0132×10^5 Pa.

When phases are at equilibrium at the triple point,

$$P_{liq}^0 = P_s^0 \quad (11.10)$$

where P_{liq}^0 and P_s^0 stand for the pressure of the substance's saturated vapour over the liquid and solid phases, respectively. At the triple point, the heats of sublimation, fusion, and evaporation are related as follows:

$$\Delta H_{\text{subl}} = \Delta H_{\text{evap}} + \Delta H_{\text{fus}} \quad (11.11)$$

The temperature dependence of the heat of phase change is given by the equation

$$\frac{\partial (\Delta H_{p.c.})}{\partial T} = \Delta C_{p.c.} = C^\alpha - C^\beta \quad (11.12)$$

in which C^α and C^β are the heat capacities of the phases α and β which are at equilibrium.

Within a narrow temperature range $\Delta C_{p.c.} = \text{const}$, then

$$\Delta H_{T.p.c.} = \Delta H_0 + \Delta C_{p.c.} T \quad (11.13)$$

or

$$\Delta H_{T_2, p.c.} = \Delta H_{T_1, p.c.} + \Delta C_{p.c.} (T_2 - T_1) \quad (11.14)$$

The equation for the temperature dependence of the saturated vapour pressure (in the case of solid and liquid phases), derived with due account for Eqs. (11.5) and (11.13), takes the form

$$\log P = -\frac{\Delta H_0}{2.3RT} + \frac{\Delta C_{p.c.}}{R} \log T + \text{const} \quad (11.15)$$

or

$$\log P = A - \frac{B}{T} + D \log T \quad (11.16)$$

where ΔH_0 is the integration constant, and A , B , and D are constants.

Exercises

1. The density of solid phenol is 1072 kg/m^3 , that of liquid phenol is 1056 kg/m^3 , the heat of its fusion is $1.044 \times 10^5 \text{ J/kg}$, and its freezing point is 314.2 K . Calculate dP/dT and the melting point of phenol at $5.065 \times 10^7 \text{ Pa}$.

Solution. Calculate dP/dT according to the Clapeyron-Clausius equation (11.4):

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H_{\text{fus}}}{T(V_{\text{liq}} - V_{\text{s}})}, \quad \Delta V = \frac{1}{d_{\text{liq}}} - \frac{1}{d_{\text{s}}} \\ \frac{dP}{dT} &= \frac{1.044 \times 10^5}{314.2 \times 0.014 \times 10^{-3}} = 2.373 \text{ Pa/K} \\ \frac{dT}{dP} &= 4.214 \times 10^{-8} \text{ K/Pa} \end{aligned}$$

To calculate the melting point at a given external pressure assume that dT/dP at pressures ranging from 1.0132×10^5 to $5.065 \times 10^7 \text{ Pa}$ is a constant quantity equal to $4.214 \times 10^{-8} \text{ K/Pa}$. Then,

$$\int_{T_1}^{T_2} dT = 4.214 \times 10^{-8} \int_{P_1}^{P_2} dP$$

and

$$T_2 = 314.2 + 4.214 \times 10^{-8} \times 5.065 \times 10^7 = 316.33 \text{ K}$$

2. Calculate the mean heat of evaporation of CH_4 at temperatures ranging from 88.2 to 113 K, proceeding from the following data:

$T, \text{ K}$	88.2	92.2	98.2	104.2	112.2
$P \times 10^{-3}, \text{ Pa}$	8	13.31	26.62	53.24	101.3

Solution. There are two ways to do the calculation:

(1) using Eq. (11.8)

$$\Delta H_{\text{evap}} = 2.3 \times 8.314 \frac{112.2 \times 88.2}{112.2 - 88.2} \log \frac{1.013 \times 10^5}{8 \times 10^3} = 8.62 \text{ kJ/mole}$$

(2) using Eq. (11.7) from which it follows that $\log P$ plotted versus $1/T$ gives a straight line (Fig. 14). The heat of evaporation can

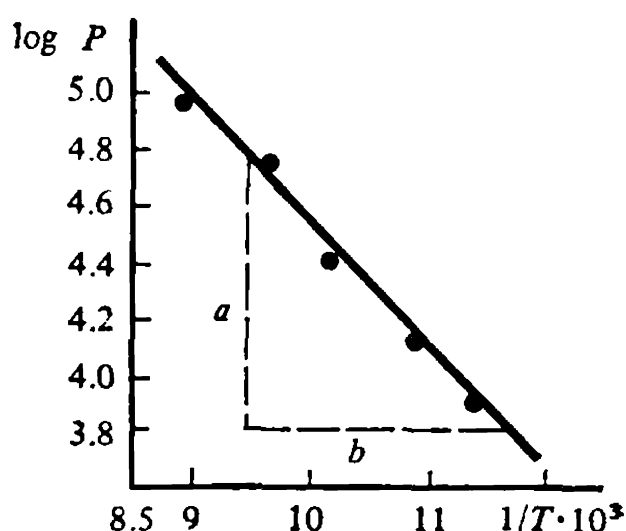


Fig. 14. $\log P$ for saturated CH_4 vapour versus inverse temperature

be defined from the slope of the straight line, which is $\tan \alpha = -\Delta H_{\text{evap}}/2.3R$. Calculate $\log P$ and $1/T$ proceeding from the following data:

$T, \text{ K}$	88.2	92.2	98.2	104.2	112.2
$P \times 10^{-3}, \text{ Pa}$	8	13.31	26.62	53.24	93.40
$(1/T) 10^3$	11.37	10.89	10.21	9.62	8.94
$\log P$	3.903	4.124	4.425	4.726	4.972

Plot $\log P$ versus $1/T$, then

$$\tan \alpha = \frac{a}{b} = \frac{0.96}{2.22 \times 10^{-3}} = -432$$

$$\Delta H_f = 432 \times 2.3 \times 8.314 = 8.27 \text{ kJ/mole}$$

This result is more reliable than the previous one because it has been calculated on the basis of five experiments (the true heat of evaporation of methane at the normal boiling point is 8.19 kJ/mole).

3. Calculate the heat of evaporation of diethyl ether using the Clapeyron-Clausius and Trouton's equations if $dP/dT = 3.53 \times 10^3 \text{ Pa/K}$ at the normal boiling point (307.9 K). Compare the result with the value given in the handbook.

Solution. Calculate the heat of evaporation using Eq. (11.5) and assuming that the vapours behave as ideal gases and that $\Delta V \approx V_v$:

$$\Delta H_{\text{evap}} = 3.53 \times 10^3 \times 8.314 \times 307.9^2 \frac{1}{1.013 \times 10^5} = 2.74 \times 10^4 \text{ J/mole}$$

Use Eq. (11.9) to find ΔH_{evap} :

$$\Delta H_{\text{evap}} = 307.9 \times 21.00 = 6470 \text{ cal/mole}$$

or

$$\Delta H_{\text{evap}} = 6470 \times 4.187 = 2.72 \times 10^4 \text{ J/mole}$$

According to the handbook, $\Delta H_{\text{evap}} = 2.67 \times 10^4 \text{ J/mole}$ —that is, the deviation from the true value as a result of calculation using approximate equations is 5.5%.

4. The temperature dependence of vapour pressure (mm Hg) in the case of liquid metallic zinc is given by the equation

$$\log P = -\frac{6997}{T} - 1.2 \log T + 12.247$$

Calculate the heat of evaporation (ΔH_{evap}) of zinc at the melting point (692.7 K).

Solution. To calculate the heat of evaporation of zinc at 692.7 K use Eq. (11.5) transforming it to

$$\Delta H_{\text{evap}} = \left(\frac{d \ln P}{dT} \right) RT^2$$

The equation for the temperature dependence of the liquid metallic zinc vapour pressure takes the form

$$\ln P = -\frac{6997 \times 2.3}{T} - 1.2 \ln T + 12.247 \times 2.3$$

Its differentiation gives

$$\frac{d \ln P}{dT} = \frac{6997 \times 2.3}{T^2} - \frac{1.2}{T}$$

Calculate ΔH_{evap} at 692.7 K:

$$\begin{aligned} \Delta H_{\text{evap}} &= 6997 \times 2.3 \times 8.314 - 1.2 \times 8.314 \times 692.7 \\ &= 126.887 \text{ kJ/mole} \end{aligned}$$

5. The temperature dependence of the saturated formic acid vapour pressure (mm Hg) is given by the equation:

$$\text{for the solid phase: } \log P = 12.486 - \frac{3160}{T}$$

$$\text{for the liquid phase: } \log P = 7.884 - \frac{1860}{T}$$

Calculate the triple point (tr.p.) coordinates.

Solution. Since the condition $P_{\text{liq}}^0 = P_s^0$ applies to phase equilibrium at the triple point, equate the reduced equations and calculate $T_{\text{tr.p.}}$ and $P_{\text{tr.p.}}^0$:

$$12.486 - \frac{3160}{T_{\text{tr.p.}}} = 7.884 - \frac{1860}{T_{\text{tr.p.}}}, \quad \text{hence } T_{\text{tr.p.}} = 282.6 \text{ K}$$

$$\log P_{\text{tr.p.}} = 7.884 - \frac{1860}{282.6} = 1.302, \quad \text{hence } P_{\text{tr.p.}} = 20 \text{ mm Hg } (2.666 \times 10^3 \text{ Pa})$$

6. Calculate the heat of sublimation of metallic zinc if the heat of its fusion (ΔH_{fus}) at the triple point temperature (692.7 K) is 6.908 kJ/mole, and the temperature dependence of the heat of evaporation is given by the equation

$$\Delta H_{\text{evap}} = 133\,738.66 - 9.972T \text{ (J/mole)}$$

Solution. According to Eq. (11.11),

$$\Delta H_{\text{subl}} = \Delta H_{\text{evap}} + \Delta H_{\text{fus}}$$

Calculate ΔH_{evap} :

$$\Delta H_{\text{evap}} = 133\,738.66 - 9.972 \times 692.7 = 126.825 \text{ kJ/mole}$$

Calculate ΔH_{subl} :

$$\Delta H_{\text{subl}} = 126.825 + 6.908 = 133.73 \text{ kJ/mole}$$

7. Calculate the heat of phase change for $\alpha\text{-FeS} \rightarrow \beta\text{-FeS}$ at 298 K. Assume that $\Delta C = \text{const}$ at temperatures ranging from $T_{\text{p.c.}}$ to 298 K. The mean heat capacity of $\beta\text{-FeS}$ is $\bar{C}_{\beta\text{-FeS}} = 53.845 \text{ J/mole}$. Find the necessary data in the handbook.

Solution. According to Eq. (11.14),

$$\Delta H_{\text{p.c., 298}} = \Delta H_{\text{p.c., } T_{\text{p.c.}}} + \Delta C (298 - T_{\text{p.c.}})$$

$$T_{\text{p.c.}} = 411 \text{ K}, \quad \bar{C}_{\alpha} = 54.85 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\Delta C = C_{\beta} - C_{\alpha} = 53.84 - 54.85 = -1.005 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\Delta H_{\text{p.c., 411}} = 4396.35 \text{ J/mole}$$

$$\Delta H_{\text{p.c., 298}} = 4396.35 - 1.005 (298 - 411) = 4509.9 \text{ J/mole}$$

8. Air is bubbled through methanol and becomes saturated with its vapour. After 1 litre of air has been passed through CH_3OH , the mass of the latter decreased by 0.201 g. The total pressure in the system is invariable and equal to $1.0132 \times 10^5 \text{ Pa}$. Calculate the saturated methanol vapour pressure at 294.5 K.

Solution. Write two equations:

$$VP = V' (P - P_{\text{CH}_3\text{OH}}^s); \quad 1 \times 1 = V' (1 - P_{\text{CH}_3\text{OH}}^s) \quad (1)$$

and

$$\left(\frac{m_{\text{CH}_3\text{OH}}}{M_{\text{CH}_3\text{OH}}} \right) RT = V' P_{\text{CH}_3\text{OH}}^0 \quad (2)$$

where V is the volume of the air before it was passed through CH_3OH , V' is the total volume of the air and CH_3OH vapour after the air has been passed through, P is the pressure of the air before it was passed through methanol, $P = 1$ atm, and $(P - P_{\text{CH}_3\text{OH}}^0)$ is the pressure of the air after it has been passed through methanol.

Divide Eq. (1) by Eq. (2) and solve them for $P_{\text{CH}_3\text{OH}}^0$:

$$P_{\text{CH}_3\text{OH}}^0 = \frac{(m/M) RT}{1 + (m/M) RT} = \frac{(0.201/32) 0.082 \times 294.4}{1 + (0.201/32) 0.082 \times 294.4} = 0.1315 \text{ atm } (1.146 \times 10^4 \text{ Pa})$$

9. Calculate $S_{(\text{H}_2\text{O}, \text{v})298}^\circ$ if $S_{(\text{H}_2\text{O}, \text{liq})298}^\circ = 69.96 \text{ J mole}^{-1} \text{ K}^{-1}$.

Solution. For the purposes of calculation assume that the process of evaporation of liquid water at a pressure of $1.0132 \times 10^5 \text{ Pa}$ comprises two steps: (a) equilibrium evaporation at a pressure equal to that of saturated vapour, ΔS_{evap} , and (b) equilibrium compression ΔS_{comp} of the saturated vapour to a pressure of 1 atm. Then,

$$\Delta S = \Delta S_{\text{evap}} + \Delta S_{\text{comp}} \quad (1), \quad S_{\text{H}_2\text{O}, \text{v}}^\circ = S_{\text{H}_2\text{O}, \text{liq}}^\circ + \Delta S \quad (2)$$

According to Eqs. (7.14) and (7.9),

$$\Delta S_{\text{evap}} = \frac{\Delta H_{\text{evap}}}{T}, \quad \Delta S_{\text{comp}} = -R \ln \frac{1}{P_{\text{H}_2\text{O}}^0}$$

To determine ΔH_{evap} find the heats of water formation for different states of aggregation at 298 K in the handbook:

$$\Delta H_{\text{evap}} = \Delta H_{\text{H}_2\text{O}, \text{v}}^\circ - \Delta H_{\text{H}_2\text{O}, \text{liq}}^\circ = -241.84 - (-285.84) = 44.00 \text{ kJ/mole}$$

as well as the saturated vapour pressure $P_{\text{H}_2\text{O}}^0 = 3.167 \times 10^3 \text{ Pa}$. Substitution of the numerical values and calculations give

$$\Delta S = \frac{44\,000}{298} - 8.314 \times 2.3 \log \frac{760}{29.76} = 118.87 \text{ J mole}^{-1} \text{ K}^{-1}$$

and the absolute entropy of the vapour is

$$S_{\text{H}_2\text{O}, \text{v}}^\circ = 69.96 + 118.87 = 188.83 \text{ J mole}^{-1} \text{ K}^{-1}$$

10. At 268.2 K, the saturated vapour pressure over solid benzene is 2279.8 Pa, and over supercooled (liquid) benzene it is 2639.7 Pa. Calculate the change in Gibbs' energy during solidification of one mole of supercooled benzene at the above temperature (assuming that the benzene vapour is an ideal gas) and indicate whether the process is reversible or not.

Solution. Since the change in Gibbs' energy (ΔG) is independent of the path of the process, assume that the solidification process com-

prises three steps: (a) reversible evaporation of liquid benzene at 2639.7 Pa; (b) reversible expansion of the vapour up to 2279.8 Pa; and (c) reversible condensation of the vapour into the solid phase. Then,

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$$

Since the first and third steps proceed at constant P and T in a reversible manner, $\Delta G_1 = \Delta G_3 = 0$, and

$$\Delta G_2 = RT \ln (P_g^0/P_{\text{liq}}^0) \quad \text{or}$$

$$\Delta G_2 = \Delta G = 8.314 \times 268.2 \times 2.3 \log \frac{2279.8}{2639.7} = -326.84 \text{ J/mole}$$

The result indicates that the process is irreversible.

11. The pressure of saturated water vapour at 428.2 K is 54.3×10^4 Pa and its specific volume is $0.3464 \text{ m}^3/\text{kg}$. Calculate the fugacity of water which is at equilibrium with its saturated vapour at 428.2 K.

Solution. According to Eq. (11.2), the fugacity of a liquid equals that of its saturated vapour, and since the pressure is relatively low, the fugacity of the saturated vapour can be calculated using Eq. (9.15):

$$f = \frac{P^2}{P_{\text{ld}}} = P^2 \frac{V}{RT} = (54.3 \times 10^4 \text{ Pa})^2 \frac{0.3464 \text{ (m}^3/\text{kg}) 18.02}{8.315 \text{ (J mole}^{-1} \text{ K}^{-1}) 428.2 \text{ (K)}} = 5.16 \times 10^5 \text{ Pa}$$

Problems

1. Can rhombic, monoclinic, liquid, and gaseous sulphur be in the state of equilibrium at 386.5 K (phase change temperature)?

2. Plot a P vs T curve for a substance existing in two solid modifications Q and R as well as in the liquid and gaseous states. The following is known about the phase state of the system:

Point	$t, ^\circ\text{C}$	$P, \text{ atm}$	Phases
1	10	1	$Q, R, \text{ vapour}$
2	30	10	$R, \text{ liquid, vapour}$
3	50	100	$Q, R, \text{ liquid}$

3. The heat of fusion and densities of liquid and solid mercury at the triple point temperature (234.29 K) are, respectively, $11.8 \times 10^3 \text{ J/kg}$, 13 690, and 14 193 kg/m^3 . Calculate the pressure at which the melting point becomes equal to 235.29 K.

4. Use two methods to calculate the heat of evaporation of water at 273.2 and 573.2 K, proceeding from the following data:

Method 1

T , K	273.16	573.16
v_v , litre/g	206.3	0.0215
v_{liq} , cm ³ /g	1.000	1.400
dP/dT	0.333 mm Hg/deg	1.201 atm/deg

Method 2

T , K	273.2	274.2	572.7	574.3
P_{sat} , H ₂ O	4.579 mm Hg	4.924 mm Hg	88.14 atm	90.17 atm

Explain why the results coincide at 273.2 K as opposed to 573.2 K when they do not.

5. Determine the boiling point of chlorobenzene at 266.6 Pa if its normal boiling point is 405.4 K and if at 5.332×10^4 Pa it boils at 382.2 K. Calculate the heat of evaporation as well as the changes in entropy, internal energy, Gibbs' and Helmholtz' energies during evaporation of one mole of chlorobenzene at the normal boiling point.

6. Calculate the coefficients A and B in the equation $\log P = A - B/T$ for the temperature dependence of the saturated vapour pressure of liquid aluminium. Check the results after having calculated the boiling point under normal conditions ($T_{n.b.} = 2600$ K) if the aluminium vapour pressure at the following temperatures is known:

T , K	1734	1974	2093	2237
P , Pa	89.3	1333	3972	1.341×10^4

7. Calculate the amount of heat necessary for heating 1 kg of TiCl₄ from 298 to 423 K. Find the necessary heat capacity values in the handbook. The temperature dependence of vapour pressure (Pa) over liquid TiCl₄ is expressed by the equation

$$\log P = 8.56 - 1450/T$$

8. Calculate the heat of evaporation of chlorine at $P = 0.1013$ MPa if the equation of the temperature dependence of the saturated vapour pressure (Pa) over liquid chlorine takes the following form:

$$P = 3.58 \times 10^6 - 3.37 \times 10^4 T + 80.11 T^2$$

9. The temperature dependence of the saturated vapour pressure (Pa) for freon CCl₂F₂ is given by the equation

$$\log P = 34.5 - \frac{2406.1}{T} - 9.26 \log T + 0.0037 T$$

Determine the saturated vapour pressure, the heat of evaporation, and the changes in entropy, Gibbs' energy, and $\Delta C_{p.c.}$ during evaporation of one mole of freon at 298 K.

10. Define the coordinates of the triple point (P and T) for 1,4-dioxane $C_4H_8O_2$, the heats of its sublimation, evaporation and fusion at that point if

	Solid state		Liquid state	
T , K	260.35	272	298.16	307.0
P , mm Hg	4.18	10	41.55	60

11. Calculate the melting point, the saturated vapour pressure at the melting point, and the heat of fusion of silver, proceeding from the temperature dependence of the saturated vapour pressure (Pa), if

$$\log P = 13.892 - 1.402 \times 10^4/T \quad \text{for solid silver}$$

and

$$\log P = 13.347 - 1.334 \times 10^4/T \quad \text{for liquid silver}$$

12. Determine the molecular weight of the acetic acid vapour from the temperature dependence of the saturated vapour pressure and the specific heat of evaporation $\Delta H_{\text{evap}} = 406.83$ J/g, found calorimetrically:

T , K	363	383	403
P , mm Hg	293	583	1040

13. Calculate the difference between the water vapour and ice pressures at 272 K. The heat of fusion of ice is 334 J/g, $P_{\text{ice}} = P_{\text{water}} = 610.48$ Pa at 273.16 K.

14*. The boiling point of benzene at 0.1013 MPa is 353.3 K. Calculate the pressure at the triple point temperature (278.66 K) using Trouton's equation with the following assumptions: the heat of evaporation is independent of temperature, and the heat of evaporation is dependent on temperature but

$$\Delta C = C_v - C_{\text{liq}} = \text{const}, \quad C_v = 81.67 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$C_{\text{liq}} = 136 \text{ J mole}^{-1} \text{ K}^{-1} \text{ (at } 278.73 \text{ K and } 4.812 \times 10^3 \text{ Pa)}$$

15*. The saturated vapour pressure of a substance is 12×10^2 Pa at 408 K. At what temperature will its sublimation take place if the pressure in the system is maintained at 2.666×10^3 Pa? The calculation may be based on Trouton's equation and the assumption that the heat of evaporation is constant.

16. Calculate ΔH_{evap} of thallium chloride at the triple point temperature (704 K). Find the necessary data in the handbook. The heat of fusion ΔH_{fus} of TlCl at 704 K is 15.564 kJ/mole.

17. The relationship between the heat of fusion of potassium and pressure (atm) according to Bridgman is given by the equation

$$T = 335.65 + 1.56 \times 10^{-2}P - 6.786 \times 10^{-7}P^2 + 1.55 \times 10^{-11}P^3$$

Determine the melting point and the heat of fusion at pressures of 1.6 and 12 000 atm if $\Delta V = 0.0268 - 0.000174 (T - 335.65)$.

18. Calculate the fugacity of liquid ammonia at 362 K. Use the data in the handbook.

19. Calculate the fugacity of liquid ammonia at 238 K. The saturated ammonia vapour pressure is $P_{\text{sat}} = 0.95$ atm. The specific vapour volume is $v = 1.215$ litre/g.

20. The melting of white phosphorus is characterized by the following melting points and changes in volume as a function of pressure:

P , atm	1	1000	2000	3000	4000
T_m , °C	44.2	73.8	101.0	126.8	151.3
ΔV , ml/kg	19.3	17.9	16.6	15.4	14.2

Calculate ΔH_{fus} by plotting the experimental data at $P = 2500$ atm. May the result be considered constant at pressures ranging from 1 to 2500 atm if $(\Delta H_{\text{fus}})_{P=1} = 648.52$ J?

21. Determine the amount of heat required for the isobaric heating of 1 kg of hexane from $t_1 = 20$ °C to $t_2 = 100$ °C. The heat capacity of hexane is independent of pressure. Use the following data for the calculation:

$$(C_P)_{\text{C}_6\text{H}_{14}}^{\text{liq}} \text{ (J/g)} = 2.07317 + 3.9170 \times 10^{-3} t$$

$$(C_P)_{\text{C}_6\text{H}_{14}}^{\text{g}} \text{ (J/g)} = 1.2254 + 4.5655 \times 10^{-3} t$$

$$\log P \text{ (mm Hg)} = 7.1584 - \frac{1322.65}{240.40 + t}$$

22. The temperature dependence of the hydrogen vapour pressure between 1 atm and P_{cr} is given by the following equation:

$$P = -\frac{56.605}{T} + 3.8015 - 0.10458T + 0.0033217T^2 + 0.043219T^3$$

At $T = 27.47$ K, $\Delta H_{\text{evap}} = 375.3466$ kJ/kg; $d^{\text{g}} = 0.00613$ kg/litre; and $d^{\text{liq}} = 0.06050$ kg/litre. Are these data mutually consistent?

23. The temperature dependence of the nicotine ($\text{C}_{10}\text{H}_{14}\text{N}_2$) vapour pressure is characterized by the following parameters:

t , °C	170	185	190	200	209	221	228
P , mm Hg	100	160	180	240	300	400	500

Plot P as a function of t and determine ΔH_{evap} and ΔS_{evap} at 200 °C.

24. Given the reduced temperature dependence of the liquid bismuth vapour pressure

t , °C	470	515	575	580	610	630	705
P , mm Hg	0.03158	0.03521	0.00492	0.00502	0.01203	0.0204	0.0832

derive the linear equation for $\log P = f(1/T)$ (by the mean value method) and calculate ΔH_{evap} .

25. What is the amount of air to be passed through carbon disulphide at 720 mm Hg and 313.2 K in order to extract 30 g of the latter if ΔH_{evap} of carbon disulphide is 355.765 J/g at $T_{\text{n.b.}} = 319.7$ K?

26. The liquid bromine vapour pressure varies with temperature as

$$\log P \text{ (mm Hg)} = -\frac{2210}{T} - 4.08 \log T + 19.82$$

Derive the equation for the temperature dependence of the heat of evaporation of bromine and calculate the change in entropy during evaporation of one mole of bromine at the boiling point (331.2 K).

27. The molar heat of evaporation of carbon tetrachloride varies with temperature as $\Delta H = 10\,960 - 10.53T$. Determine the saturated vapour pressure of CCl_4 at 333.2 K if the boiling point of CCl_4 at 1 atm is 348.2 K.

28. The temperature dependence of the ethyl ether vapour pressure is characterized by the following values:

$t, ^\circ\text{C}$	-10	0	10	20	30
$P, \text{ mm Hg}$	114.8	184.4	286.8	432.8	634.8

Plot $\log P$ versus $1/T$ and use the resulting curve to determine the molar heat of evaporation of the ether and its normal boiling point.

29. The temperature dependence of the chloroform vapour pressure is characterized by the following values:

$t, ^\circ\text{C}$	20	30	40	50	60
$P, \text{ mm Hg}$	161	248	369	535	755

Plot P as a function of T and calculate the heat of evaporation of chloroform at 40 $^\circ\text{C}$.

30. The temperature dependence of the saturated aluminium vapour pressure is characterized by the following values:

$T, \text{ K}$	1734	1974	2093	2237
$P, \text{ mm Hg}$	0.67	10.00	29.8	100.6

Using the $\log P$ versus $1/T$ plot, calculate the boiling point of aluminium at 560 mm Hg and derive the linear equation for $\log P$ as a function of $1/T$.

31. Air is saturated with water vapour at 25 $^\circ\text{C}$. At what temperature will the relative humidity of air, at an invariable water vapour content, be equal to 80% if the water vapour pressure at 25 $^\circ\text{C}$ is 23.76 mm Hg and the specific heat of water evaporation is $-280\,090.8$ J/g?

Multivariant Problems

1. Given the temperature dependence of the saturated vapour pressure and the density of substance A with molecular weight M in the solid and liquid states (d_s and d_{liq} in kg/m^3) at the triple point

Variant	Solid state		Liquid state		Conditions
	T, K	P, Pa	T, K	P, Pa	
1	268.2	401.2	269.2	505	$M = 18$
	269.2	437.2	272.2	533.2	$P = 40.5 \times 10^5 \text{ Pa}$
	270.2	475.9	273.2	573	
	271.2	517.2	275.2	656	$d_s = 918$
	272.2	533.3	278.2	760	
			283.2	982	$d_{llq} = 1000$
			288.2	1 600	
2	248.0	7 998	260.0	23 327	$M = 27$
	254.4	13 300	265.0	27 190	$P = 800 \times 10^5 \text{ Pa}$
	258.0	17 995	270.0	31 860	$d_s = 718$
	259.0	19 995	278.0	40 290	$d_{llq} = 709$
	260.0	23 327	282.0	47 990	
3	55	1 333	60.0	12 663	$M = 28$
	58	3 999	64.0	17 329	$P = 500 \times 10^5 \text{ Pa}$
	59.2	11 997	66.0	22 394	$d_s = 1026$
	63	14 663	67.8	27 993	$d_{llq} = 808$
	64	17 329	69.0	31 992	
4			71.0	39 990	
	100	4 132	105	17 329	$M = 30$
	104	8 531	112	29 653	$P = 900 \times 10^5 \text{ Pa}$
	107	14 663	114	34 738	$d_s = 1272$
	109	19 995	115	38 657	
	110.5	25 367	116	46 435	$d_{llq} = 1260$
5	112	29 653	117	53 053	
	229.2	133.3	273.2	4 786	$M = 32$
	248.0	694.5	282.5	6 665	$P = 300 \times 10^5 \text{ Pa}$
	257.0	1 333	298.2	12 697	$d_s = 837$
	267.2	2 966	306.7	16 396	
	273.2	4 786	312.5	18 929	$d_{llq} = 825$
			316.5	21 328	

(Table continued)

Variant	Solid state		Liquid state		Conditions
	T, K	P, Pa	T, K	P, Pa	
6	173	7 330	190	31 192	$M = 34$
	178	11 600	196	38 657	$P = 450 \times 10^5 \text{ Pa}$
	183	16 795	200	46 655	$d_s = 1010$
	184	19 995	207	55 986	$d_{llq} = 980$
	190	31 192	215	69 476	
			221	77 314	
7	196	101 325	212	592 751	$M = 44$
	203	190 491	220	648 480	$P = 750 \times 10^5 \text{ Pa}$
	213	402 360	223	674 824	$d_s = 1542$
	220	648 480	239	1 005 114	$d_{llq} = 1510$
			241	1 065 237	
			242	1 131 722	
8	276.6	1 413	277.2	1 826	$M = 46$
	278.2	1 706	279.2	2 082	$P = 950 \times 10^5 \text{ Pa}$
	279.2	1 879	281.4	2 372	$d_s = 1240$
	280.2	2 066	283.2	2 626	$d_{llq} = 1290$
	281.4	2 372	285.2	2 932	
			288.7	3 279	
9	230	26 260	236	63 315	$M = 52$
	233	31 458	246	78 647	$P = 350 \times 10^5 \text{ Pa}$
	237	39 990	248	83 979	$d_s = 3010$
	240	49 997	249	86 645	$d_{llq} = 2955$
	243	58 518	252.5	96 942	
	245	66 650	253.5	100 508	
	249	86 645			
10	1 758.2	22.66	1832	187	$M = 52.5$
	1 788.2	63.98	1873.2	300	$P = 500 \times 10^5 \text{ Pa}$
	1 810.2	99.97	1905	387	$d_s = 6800$
	1 835.2	115.99	1938	486	$d_{llq} = 6750$
	1 873.2	300.00	1956	573	
			1991	800	
			2040	973	

(Table continued)

Variant	Solid state		Liquid state		Conditions
	T, K	P, Pa	T, K	P, Pa	
11	242.1	1 333	293	26 660	$M = 58$
	252.4	2 666	303	37 724	$P = 700 \times 10^5 \text{ Pa}$
	263.8	5 332	308	46 188	$d_s = 822$
	271.2	7 998	311	51 720	$d_{lq} = 812$
	280.9	13 330	313	56 186	
	293.0	26 660	316	63 317	
12	183.2	333.3	201	4 665.5	$M = 64$
	188.0	586.5	203.7	5 305	$P = 1000 \times 10^5 \text{ Pa}$
	196.2	1 850	214	7 198	$d_s = 1600$
	199.2	3 000	216	7 998	$d_{lq} = 1560$
	203.7	5 305	230.2	13 328	
			244.0	21 728	
13	131	1 333	137	6 665	$M = 68$
	135	1 999.5	141	7 331.5	$P = 300 \times 10^5 \text{ Pa}$
	137	2 666	145	8 664.5	$d_s = 1450$
	139.2	3 999	146	9 997.5	$d_{lq} = 1434$
	141.5	5 332	149	12 663	
	144.0	7 998	151.4	15 996	
	146	9 997.5			
14	273.2	3 265.8	274.2	3 730	$M = 78$
	274.2	3 465.8	275.2	4 000	$P = 900 \times 10^5 \text{ Pa}$
	276.2	3 932.3	276.2	4 160	$d_s = 893$
	277.2	4 305.6	278.2	4 530	$d_{lq} = 890$
	278.2	4 530	283.2	6 050	
			290.2	8 930	
15	177.3	15 996	180	26 660	$M = 81$
	180	19 995	185.5	32 992	$P = 300 \times 10^5 \text{ Pa}$
	182	23 994	188	37 057	$d_s = 1626$
	184	28 659	191	43 456	$d_{lq} = 1610$
	185.5	32 992	194	51 987	
			196.8	59 985	

(Table continued)

Variant	Solid state		Liquid state		Conditions
	T, K	P, Pa	T, K	P, Pa	
16	99	10 675	111	63 984	$M = 83.5$
	101.9	13 995	115.5	68 649	$P = 800 \times 10^5 \text{ Pa}$
	103	17 330	117	72 782	$d_s = 3330$
	104.5	19 995	118	77 980	$d_{llq} = 2150$
	107.2	26 660	119	82 646	
	115.5	68 649	119.6	87 711	
17	272.5	3 332.5	275.7	4 878.8	$M = 84$
	273.4	3 599.1	280.2	5 598.6	$P = 120 \times 10^5 \text{ Pa}$
	275.7	4 065.6	281.7	5 798.6	$d_s = 796$
	277.2	4 398.9	283.3	6 198.6	$d_{llq} = 788$
	279.2	5 065.4	285.2	6 931.6	
	281.7	5 798.6	287.5	7 731.4	
18	353.2	39.99	363.2	186.6	$M = 122$
	363.2	79.98	393.2	679.8	$P = 850 \times 10^5 \text{ Pa}$
	373.2	186.6	395.2	733.1	$d_s = 1105$
	383.2	393.2	400.7	973.1	$d_{llq} = 1095$
	393.2	679.8	403.7	1 133	
			408.7	1 399.6	
19	205.2	16 796	219.2	55 319	$M = 127.5$
	208	19 195	224.2	59 985	$P = 500 \times 10^5 \text{ Pa}$
	209.2	22 662	226.7	66 650	$d_s = 2970$
	213.2	29 859	229.2	75 981	$d_{llq} = 2850$
	216.4	35 991	231.2	83 979	
	220.0	45 988	323.7	87 975	
	224.2	59 985			
20	334.6	266.6	248.2	1 046	$M = 127.5$
	338.4	352.2	353.7	1 266.3	$P = 180 \times 10^5 \text{ Pa}$
	343.2	533.2	358.2	1 399	$d_s = 1145$
	348.2	733.1	363.8	1 666	$d_{llq} = 982$
	353.2	1 039.7	368.8	4 066	
	353.7	1 266.3	373.8	2 466	

(Table concluded)

Variant	Solid state		Liquid state		Conditions
	T, K	P, Pa	T, K	P, Pa	
21	423.5	23 994	446.4	47 000	$M = 152$ $P = 600 \times 10^5 \text{ Pa}$ $d_s = 985$ $d_{llq} = 977$
	433.2	31 325	448.2	47 454	
	437.7	35 324	451.2	49 987	
	441.2	39 323	460	55 986	
	444.2	43 322	470	63 317	
	448.2	47 454	480	71 345	
22	223.2	133.3	244.2	1 200	$M = 154$ $P = 60.8 \times 10^5 \text{ Pa}$ $d_s = 1680$ $d_{llq} = 1650$
	237.2	466.5	253.2	1 319	
	246.2	799.8	270.1	2 465	
	252.2	1 213	282.5	3 865	
	253.2	1 319	285.7	4 398	
23	418.0	133.3	490.5	5 332	$M = 174$ $P = 220 \times 10^5 \text{ Pa}$ $d_s = 954$ $d_{llq} = 948$
	446.5	667.0	504.8	8 020	
	460.2	1 333.0	523.0	13 300	
	474.9	2 666.0	552.0	26 660	
	490.5	5 332.0	583.2	53 320	
			612.0	101 308	
24	377.2	7 064	373.2	10 662	$M = 254$ $P = 220 \times 10^5 \text{ Pa}$ $d_s = 3 960$ $d_{llq} = 3 900$
	381.2	8 531	388.2	12 397	
	383.2	9 331	392.2	13 997	
	386.2	10 397	393.2	14 796	
	389.7	11 997	397.2	16 929	
	392.2	13 997	401.2	19 462	

(tr.p.): (1) plot $\log P$ as a function of $1/T$; (2) determine the triple point coordinates on the plot; (3) calculate the mean heats of evaporation and sublimation; (4) plot the temperature dependence of the saturated vapour pressure; (5) determine the heat of fusion of the substance at the triple point temperature; (6) calculate dT/dP for the melting process at the triple point temperature; (7) calculate the melting point of the substance at pressure P , Pa; (8) calculate the changes in entropy, Gibbs' and Helmholtz' energies, enthalpy, and internal energy during sublimation of one mole of the substance at the triple point; (9) determine the number of thermodynamic degrees of freedom at the following temperatures and pressures: (a)

$T_{\text{tr.p.}}$, $P_{\text{tr.p.}}$; (b) $T_{\text{n.b.}}$, $P = 1 \text{ atm}$; and (c) $T_{\text{n.b.}}$, $P_{\text{tr.p.}}$. Find the necessary values in the table on pp. 178-182.

2. The following parameters are known for substance A: the heat of evaporation, the heat of sublimation, and the densities of the solid and liquid phases, d_s and d_{liq} , at the triple point temperature $T_{\text{tr.p.}}$. Proceeding from these data: (1) calculate the boiling point of substance A using Trouton's equation; (2) derive the equation $\log P_{\text{liq}} = \frac{a}{T} + b$, where a and b are constants for the liquid \rightleftharpoons vapour equilibrium; (3) use the derived equation to calculate the saturated vapour pressure of substance A at the triple point; (4) derive the equation $\log P_s = \frac{a'}{T} + b'$ for the solid phase \rightleftharpoons vapour equilibrium; (5) calculate dP/dT for the solid phase \rightleftharpoons liquid equilibrium; and (6) plot the equilibrium pressure as a function of the phase change temperature for the three phase states at pressures ranging from 0 to $1.013 \times 10^5 \text{ Pa}$. In this pressure range, the temperature dependence of pressure for the solid phase \rightleftharpoons liquid phase equilibrium is a straight line on the plot; that is, $dP/dT = \text{const.}$

Variant			Substance A	$T, \text{ K}$	Heat of evaporation, $10^{-4}, \text{ J/mole}$	Heat of sublimation, $10^{-4}, \text{ J/mole}$	$d_s \times 10^{-3}, \text{ kg/m}^3$	$d_{\text{liq}} \times 10^{-3}, \text{ kg/m}^3$
1	12	23	Zn	692.6	12.14	12.84	6.914	6.920
2	13	24	Cu	1356.1	32.09	33.39	8.41	8.37
3	14	25	Ag	1234.1	25.54	26.67	9.68	9.32
4	15		K	336.65	8.77	8.99	0.851	0.830
5	16		Bi	644.15	17.42	18.50	9.35	10.24
6	17		Hg	234.35	6.45	6.68	14.19	13.69
7	18		KF	1159.1	18.04	20.68	2.43	1.914
8	19		I ₂	386.7	4.53	6.08	4.82	3.97
9	20		Br ₂	266	3.22	4.27	3.14	2.93
10	21		NH ₃	199.15	2.41	3.18	0.81	0.664
11	22		CH ₃ COOH	256.4	2.97	4.12	1.266	1.053

3. Substance A evaporates at temperature T . Calculate the specific heat of evaporation at this temperature. Write the equation for the temperature dependence of the heat of evaporation of substance A. Find the heat capacities of the saturated vapour in the liquid in the handbook, assuming that they are constant in the given temperature range. The heats of evaporation at the normal boiling point are given in the table on p. 184.

Variant		Substance A	$T_{n.b.}$ K	ΔH_{evap} at $T_{n.b.}$ kJ/mole	T , K	
1	11	TiCl ₄	409	35.75	309	460
2	12	HNO ₃	357	38.2	300	400
3	13	Br ₂	331.5	29.6	270	400
4	14	H ₂ O	373.2	40.7	300	450
5	15	CS ₂	319.5	26.8	250	370
6	16	CCl ₄	350	30.0	300	400
7	17	Hg	630	59.3	550	700
8	18	CH ₂ O ₂ , formic acid	373.6	22.3	320	400
9	19	CH ₄ O, methanol	338	35.3	300	400
10	20	C ₂ H ₄ O ₂ , acetic acid	391	45.0	320	450
11	21	C ₂ H ₆ O, ethanol	351.5	39.5	300	400
12	22	C ₃ H ₆ O, acetone	329.3	98.3	280	370
13	23	C ₆ H ₆ , benzene	353.2	30.8	300	400
14	24	C ₇ H ₈ , toluene	384	33.2	320	450
	25	n-C ₆ H ₁₄ , hexane	342	28.9	290	

4. Dry air occupying volume V at temperature T_1 and pressure P has been passed over substance A at temperature T_2 and become saturated with the vapour of this substance. What will the change in the mass of the substance be after having passed the air over it? The vapour pressure of substance A at T_2 has been taken from the tables in the handbook. Remember that the total pressure in the system remains invariable throughout the process and equal to P (use the table on p.185).

5*. During dispersion in dry air at temperature T , substance A evaporated, formed saturated vapour at an invariable total pressure of 1 atm, and cooled the air. By how many degrees has the air temperature gone down? Assume for the purposes of the calculation that in the temperature range under consideration: (1) N₂, O₂, and

Variant	T , K	Substance A	Variant	T , K	Substance A	Variant	T , K	Substance A
1	303	H ₂ O	3	288	CH ₂ O ₂ , formic acid	5	293	C ₄ H ₁₀ O, diethyl ether
2	298	CCl ₄	4	283	CH ₄ O, methanol	6	308	C ₃ H ₆ O, acetone

Variant	T_1, K	$P \times 10^{-4}, Pa$	V, m^3	Substance A	T_2, K	Variant	T_1, K	$P \times 10^{-4}, Pa$	V, m^3	Substance A	T_2, K
1	283	9.91	3	H ₂ O	363	14	191	9.85	7	CH ₃ OH	293
2	285	9.97	4	H ₂ O	353	15	293	9.91	9	CH ₃ OH	288
3	287	10.05	5	H ₂ O	343	16	293	10.05	7	CH ₃ COCH ₃	323
4	289	11.12	6	H ₂ O	333	17	295	10.12	8	CH ₃ COCH ₃	318
5	291	9.71	7	H ₂ O	323	18	297	9.71	9	CH ₃ COCH ₃	313
6	299	9.78	8	CCl ₄	333	19	299	9.78	10	CH ₃ COCH ₃	308
7	295	9.85	9	CCl ₄	318	20	301	9.85	2	CH ₃ COCH ₃	303
8	297	9.91	10	CCl ₄	313	21	283	9.71	2	C ₆ H ₆	343
9	299	9.97	2	CCl ₄	308	22	285	9.78	3	C ₆ H ₆	333
10	301	10.05	3	CCl ₄	303	23	287	9.85	4	C ₆ H ₆	323
11	285	10.12	4	CH ₃ OH	308	24	289	9.91	5	C ₆ H ₆	313
12	287	9.71	5	CH ₃ OH	303	25	291	9.97	6	C ₆ H ₆	303
13	289	9.78	6	CH ₃ OH	298						

the vapour of A are ideal gases; (2) the heat capacity of N_2 , O_2 , and the vapour of A is constant; and (3) calculate the heat of evaporation of A using the tabulated temperature dependence of the saturated vapour pressure.

The problem is to be solved graphically, the answer to variant 1 being $\Delta T = -19 \pm 1$ K.

CHAPTER 12

Thermodynamic Characteristics of Solutions and Processes of Their Formation

Basic Equations and Symbols

The concentrations of two-component solutions can be expressed in a number of ways:

in terms of weight ratio,

$$w_i = m_i/m \quad (12.1)$$

where m_i is the weight of the i th component in the solution, and m is the weight of the solution;

in terms of weight percentage,

$$w_i \times 100 = m_i \times 100/m$$

in terms of molar ratio,

$$r_i = n_1/n_2 \quad (12.2)$$

where n_1 is the number of moles of solvent, and n_2 is the number of moles of solute;

in terms of molar fraction,

$$x_i = n_i/(n_1 + n_2) \quad (12.3)$$

and in terms of mole percentage,

$$x_i \times 100 = \frac{n_i \times 100}{n_1 + n_2}$$

Molality m is the number of moles (n_2) of solute per 1000 g of solvent. Molarity c is the number of moles (n_2) of solute per litre of solution.

The mean molecular weight \bar{M} of a solution is calculated using the equation

$$\bar{M} = x_1 M_1 + x_2 M_2 \quad (12.4)$$

The partial molar quantities \bar{L}_i are determined from the equation

$$\bar{L}_i = \left(\frac{\partial L_{\text{total}}}{\partial n_i} \right)_{P, T, n_j} \quad (12.5)$$

in which L_{total} is the total (mean) extensive property of the solution, and n_j corresponds to $n_1, n_2, n_3, \dots, n_k$.

The partial molar quantities may be volume, enthalpy, entropy, Gibbs' and Helmholtz' energies:

$$\begin{aligned}\bar{V}_i &= \left(\frac{\partial V}{\partial n_i} \right)_{P,T,n_j}, \quad \bar{H}_i = \left(\frac{\partial H}{\partial n_i} \right)_{P,T,n_j} \\ \bar{S}_i &= \left(\frac{\partial S}{\partial n_i} \right)_{P,T,n_j}, \quad \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j}\end{aligned}$$

where $\bar{V}_i, \bar{H}_i, \bar{S}_i$, and \bar{G}_i are the partial molar volume, enthalpy, entropy, and Gibbs' energy, respectively. The partial molar Gibbs' energy of the i th component corresponds to its chemical potential:

$$\bar{G}_i = \mu_i \quad (12.6)$$

The temperature derivative of the chemical potential of the i th component corresponds to its partial molar entropy:

$$\bar{S}_i = - \left(\frac{\partial \mu_i}{\partial T} \right)_P \quad (12.7)$$

where μ is the chemical potential.

The partial molar displacement functions ΔL_i^m (relative partial molar quantities) are determined as follows:

$$\Delta L_i^m = \bar{L}_i - L_i^\circ \quad (12.8)$$

where L_i° is the extensive function L of the i th component in the standard state. The partial molar functions of mixing include

$$\begin{aligned}\Delta V_i^m &= \bar{V}_i - V_i^\circ, \quad \Delta H_i^m = \bar{H}_i - H_i^\circ, \\ \Delta S_i^m &= \bar{S}_i - S_i^\circ, \quad \Delta G_i^m = \bar{G}_i - G_i^\circ\end{aligned}$$

where ΔH_i^m is the enthalpy of mixing of the i th component, also referred to as the differential heat of solution. Gibbs' energy of mixing is

$$\Delta G_i^m = \Delta \mu_i = \mu_i - \mu_i^\circ \quad (12.9)$$

where μ_i° is the chemical potential of the i th component in the standard state, and the entropy of mixing is

$$\Delta S_i^m = - \left(\frac{\partial \Delta \mu_i}{\partial T} \right)_P \quad (12.10)$$

The ratio between the partial molar quantities is given by the Gibbs-Duhem equations:

$$L_{\text{total}} = \bar{L}_1 n_1 + \bar{L}_2 n_2 \quad (12.11)$$

$$L = \frac{L_{\text{total}}}{n_1 + n_2} = \bar{L}_1 x_1 + \bar{L}_2 x_2 \quad (12.12)$$

$$\bar{L}_1 = L - \left(\frac{\partial L}{\partial x_2} \right)_{P,T,x_1} x_2 \quad (12.13)$$

$$\bar{L}_2 = L + \left(\frac{\partial L}{\partial x_1} \right)_{P,T,x_2} (1 - x_2) \quad (12.14)$$

$$\Delta L_{\text{int}}^m = \Delta L_1^m n_1 + \Delta L_2^m n_2 \quad (12.15)$$

where ΔL_{int}^m is the integral function of mixing;

$$\frac{\Delta L_{\text{int}}^m}{n_1 + n_2} = \Delta L^m = \Delta L_1^m x_1 + \Delta L_2^m x_2 \quad (12.16)$$

$$\left(\frac{\partial \Delta L^m}{\partial n_i} \right)_{P,T,n_j} = \Delta L_i^m \quad (12.17)$$

For example, the equations for the entropy and heat of mixing take the form

$$\frac{S_{\text{total}}}{n_1 + n_2} = \bar{S}_1 x_1 + \bar{S}_2 x_2$$

$$\Delta H_{\text{int}}^m = n_1 \Delta H_1^m + n_2 \Delta H_2^m$$

where ΔH^m is the integral enthalpy of mixing (integral heat of solution or relative integral enthalpy);

$$\Delta H_1^m = \left(\frac{\partial \Delta H^m}{\partial n_1} \right)_{P,T} \quad (12.18)$$

$$\Delta H_2^m = \Delta H_{\infty}^m - \bar{L}_2$$

where ΔH_{∞}^m is the integral heat of solution for a finitely diluted solution (calculated by extrapolation), and \bar{L}_2 is the partial molar heat of dilution from a given concentration to that in the finitely diluted solution.

The apparent molar property L of the second component φ_L , is determined from the equation

$$L_{\text{total}} = n_1 L_1^{\circ} - n_2 \varphi_L, \quad \varphi_L = \frac{L_{\text{total}} - n_1 L_1^{\circ}}{n_2} \quad (12.19)$$

The properties of ideal solutions are given by Raoult's equation

$$P_i = P_i^{\circ} x_i^{\text{liq}} \quad (12.20)$$

in which P_i is the partial saturated vapour pressure of the i th component in the solution, P_i° is the saturated vapour pressure of the pure i th component, and x_i^{liq} is the molar fraction of the i th component in the liquid phase.

Accordingly, the functions of mixing of ideal solutions are as follows:

$$\Delta V_i^m = 0, \quad \Delta H_i^m = 0, \quad \Delta S_i^m = -R \ln x_i \quad (12.21)$$

$$\Delta G_i^m = \Delta \mu_i = RT \ln x_i \quad (12.22)$$

and the chemical potential of the i th component of an ideal (perfect) solution is

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad (12.23)$$

In the case of nonideal solutions, Raoult's equation (12.20) does not apply because $P_i \neq P_i^\circ x_i^{\text{liq}}$ and the functions of mixing of non-ideal solutions are not equal: $\Delta V_i^m \neq 0$, $\Delta H_i^m \neq 0$,

$$\Delta G_i^m = \Delta \mu_i = RT \ln a_i \quad (12.24)$$

$$\Delta S_i^m = \frac{\Delta H_i^m}{T} - R \ln a_i \quad (12.25)$$

where a_i is the activity (effective concentration) of the i th component in the solution. The activity a_i is determined from the relation $a_i = f_i/f_i^\circ$ (at P and $P^\circ \leq 1.0133 \times 10^5$ Pa):

$$a_i = P_i/P_i^\circ \quad (12.26)$$

or

$$a_i = x_i \gamma_i \quad (12.27)$$

where f_i and f_i° stand for the fugacities of the i th component in the solution and in the standard state, and γ_i is the rational activity coefficient. The chemical potential of the i th component of a non-ideal solution is determined as follows:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (12.28)$$

The activity is temperature-dependent. This dependence is given by the equations

$$\left(\frac{\partial \ln a_i}{\partial T} \right)_{P, x_i} = \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P, T} = \frac{\Delta H_i^m}{RT^2} \quad (12.29)$$

$$\log \frac{a_{i(T_2)}}{a_{i(T_1)}} = \log \frac{\gamma_{i(T_2)}}{\gamma_{i(T_1)}} = \frac{\Delta H_i^m (T_2 - T_1)}{2.3RT_2T_1} \quad (12.30)$$

The heats of solution, dilution, and mixing of solutions are given by the equation

$$q = \Delta H_f^m - \Sigma \Delta H_i^m \quad (12.31)$$

where ΔH_f^m and ΔH_i^m are the integral heats of solution for the final and initial solutions. The quantities of the solutions are taken into consideration in calculations.

Exercises

1. Calculate the mole percentage of a 60% aqueous solution of methanol.

Solution. According to Eq. (12.3),

$$x_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}}}{n_{\text{CH}_3\text{OH}} + n_{\text{H}_2\text{O}}} = \frac{m_{\text{CH}_3\text{OH}}/M_{\text{CH}_3\text{OH}}}{m_{\text{CH}_3\text{OH}}/M_{\text{CH}_3\text{OH}} + m_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}}$$

If the solution is taken in an amount of 100 g, and m_i is the weight percentage of the i th component in the solution, then

$$x_{\text{CH}_3\text{OH}} = \frac{60/32}{60/32 + 40/18} = 0.458$$

or the mole percentage of CH_3OH will be $x100 = 45.8\%$.

2. Calculate the molar fraction of HCl in one mole of an aqueous solution of HCl .

Solution. According to Eq. (12.3),

$$x_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_{\text{HCl}} + m_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}} = \frac{m}{m + 1000/18} = \frac{1}{55.55} = 0.018$$

$$n_{\text{HCl}} = m = 1, \quad m_{\text{H}_2\text{O}} = 1000 \text{ g}, \quad 1000/18 = 55.55$$

3. At 293.2 K, the density of a 60% aqueous solution of methanol is 0.8946 g/ml. Calculate the volume of one mole of the solution.

Solution. Calculate the volume of 1 g of the solution:

$$V = \frac{1}{d} = \frac{1}{0.8946} = 1.118 \text{ ml/g}$$

Calculate the mean molecular weight \bar{M} of the solution according to Eq. (12.4). Determine the molar fraction of CH_3OH from the equation

$$x_{\text{CH}_3\text{OH}} = \frac{60/32}{60/32 + 40/18} = 0.458$$

and $x_{\text{H}_2\text{O}} = 1 - 0.458 = 0.542$. Then,

$$\bar{M} = x_{\text{CH}_3\text{OH}}M_{\text{CH}_3\text{OH}} + x_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}} = 0.458 \times 32 + 0.542 \times 18 = 24.41$$

Calculate the volume of one mole of the solution:

$$V/\sum n_i = V\bar{M}$$

$$V_m = \frac{V}{\sum n_i} = 1.118 \times 24.41 = 27.29 \text{ ml/mole}$$

4. The volume of a solution, as a function of its composition, for the H_2O - NaCl system is given by the equation

$$V_{\text{total}} = 55.55V_{\text{H}_2\text{O}} + 16.4m + 2.5m^2 - 1.2m^3$$

in which m is the molality of the solute. Determine the partial and apparent molar volumes of a 0.5 M NaCl solution.

Solution. According to Eq. (12.5),

$$\bar{V}_{\text{NaCl}} = \left(\frac{\partial V}{\partial n_{\text{NaCl}}} \right)_{P, T, n_{\text{H}_2\text{O}}}$$

$$n_{\text{H}_2\text{O}} = 1000/18 = 55.55 = \text{const}, \quad n_{\text{NaCl}} = m$$

Differentiation of the original equation gives the following expression for the partial molar volume:

$$\left(\frac{\partial V_{\text{total}}}{\partial m} \right) = \bar{V}_2 = 16.4 + 5m - 3.6m^2$$

Since $m = 0.5$, then $\bar{V}_2 = 18.0$ ml/mole.

Determine the apparent molar volume using Eq. (12.19):

$$\varphi_{V_2} = (V_{\text{total}} - n_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}}^\circ) / n_{\text{NaCl}}$$

Use the equation given in the statement of the problem to calculate V_{total} which equals 1008.675. Substitution of this value into Eq. (12.19) gives

$$\varphi_{V_{\text{NaCl}}} = (1008.675 - 55.55 \times 18) / 0.5 = 17.35 \text{ ml/mole}$$

5. Calculate, using the intercept method, the partial molar volumes of water and methanol for a 60% methanol solution at 293.2 K. The calculation should be based on the following methanol solution densities as a function of concentration:

Alcohol, %	0	20	40	60	80	90	100
d , g/ml	0.9982	0.9666	0.9345	0.8946	0.8469	0.8202	0.7917

Solution. Conversion of the weight percentage into weight ratios and densities into specific volumes ($v = 1/d$) gives

CH ₃ OH, %	0	20	40	60	80	90	100
$w_{\text{CH}_3\text{OH}}$	0	0.2	0.4	0.6	0.8	0.9	1
v , ml/g	1.002	1.035	1.070	1.118	1.181	1.219	1.263

Plot $v = f(w_{\text{CH}_3\text{OH}})$ (Fig. 15). Draw a line tangent to the curve at the point corresponding to 60% CH₃OH. The intercepts on the X and Y axes give the partial specific volumes v_i : $\bar{V}_{\text{CH}_3\text{OH}} = 1.244$ ml/g, $\bar{V}_{\text{H}_2\text{O}} = 0.931$ ml/g. Find the partial molar volumes \bar{V}_i from the equation $\bar{V}_i = V_i \bar{M}_i$:

$$\bar{V}_{\text{CH}_3\text{OH}} = 1.244 \times 32 = 29.8 \text{ ml/g}$$

$$\bar{V}_{\text{H}_2\text{O}} = 0.931 \times 18 = 16.78 \text{ ml/g}$$

6. Calculate the relative ($\Delta V_{\text{CH}_3\text{OH}}^m$) and apparent ($\varphi_{V_{\text{CH}_3\text{OH}}}$) partial molar volumes of methanol in an aqueous 60% solution.

The calculation should be based on the following methanol solution densities as a function of concentration:

CH ₃ OH, %	0	20	40	60	80	90	100
$w_{\text{CH}_3\text{OH}}$	0	0.2	0.4	0.6	0.8	0.9	1
V , ml/g	1.002	1.035	1.070	1.118	1.181	1.219	1.263

Solution. Calculate the relative partial molar volume $\bar{V}_{\text{CH}_3\text{OH}}$ using the equation

$$\Delta V_{\text{CH}_3\text{OH}}^m = \bar{V}_{\text{CH}_3\text{OH}} - V_{\text{CH}_3\text{OH}}^\circ M_{\text{CH}_3\text{OH}}$$
$$\Delta V_{\text{CH}_3\text{OH}}^m = 39.36 - 1.263 \times 32 = -0.786 \text{ ml/mole}$$

To calculate the apparent molar volume $\varphi_{V_{\text{CH}_3\text{OH}}}$ use the equation

$$\varphi_{V_{\text{CH}_3\text{OH}}} = \frac{V - V^\circ x_{\text{H}_2\text{O}}}{x_{\text{CH}_3\text{OH}}}$$
$$V_m = \frac{V}{\sum n_i} = 27.90 \text{ ml/mole}$$

$V_{\text{H}_2\text{O}}^\circ = 18.02 \text{ ml/mole}$, $x_{\text{CH}_3\text{OH}} = 0.458$, $x_{\text{H}_2\text{O}} = 0.542$. Substitution of the numbers and calculations give $\varphi_{V_{\text{CH}_3\text{OH}}} = 39.60 \text{ ml/mole}$.

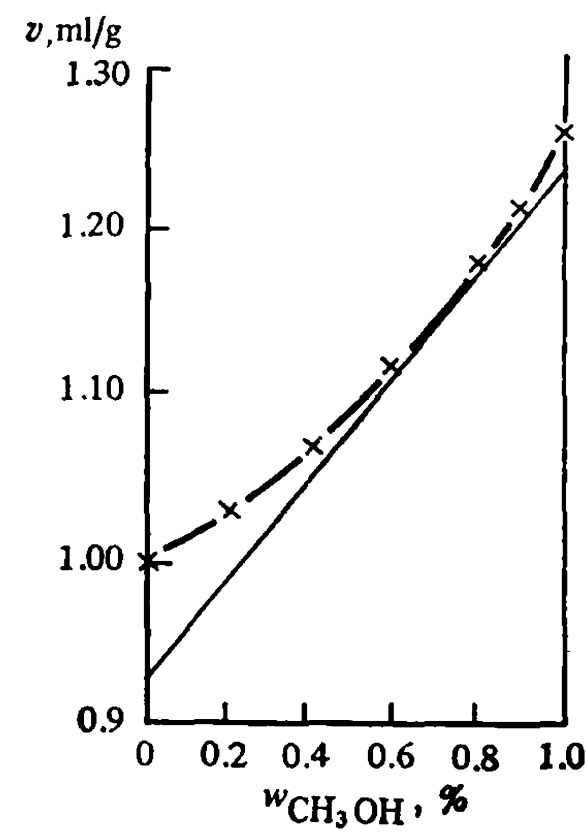


Fig. 15. Volume of CH_3OH solution in H_2O versus molar fraction

7. The following are the value of partial molar and apparent partial volumes of methanol in its aqueous solutions at 298 K:

$\bar{V}_{\text{CH}_3\text{OH}}$	0.123	0.272	0.458	0.692	0.835
$V/(n_1 + n_2)$, ml/mole	20.4	23.3	27.3	32.7	36.3
$\bar{V}_{\text{CH}_3\text{OH}}$, ml/mole	37.8	39.0	39.8	40.4	40.4
$\bar{V}_{\text{H}_2\text{O}}$, ml/mole	18.0	17.5	16.8	15.4	15.0
$\varphi_{V_{\text{CH}_3\text{OH}}}$, ml/mole	37.25	37.4	38.3	39.2	39.9

What conclusions can be drawn from the above values?

Solution. The higher the degree of dilution of a solution, the greater the difference between the partial molar volumes and the volumes of the pure components and the smaller the difference between the apparent and partial molar volumes.

8. Calculate the differential heats of solution of sulphuric acid ($Q_{\text{H}_2\text{SO}_4}$) and water ($Q_{\text{H}_2\text{O}}$) for 84.5% solution. Use the concentration dependence of the integral heat of solution at 298 K:

$r_1 = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{SO}_4}}$	0	0.5	1	1.5	2	3	4	6
$-\Delta H^m$, kJ/mole	0	15.73	27.8	35.9	41.45	48.92	53.89	60.23

Solution. The concentrations are expressed in such a manner that the number n_2 of moles of the solute remains constant, while the

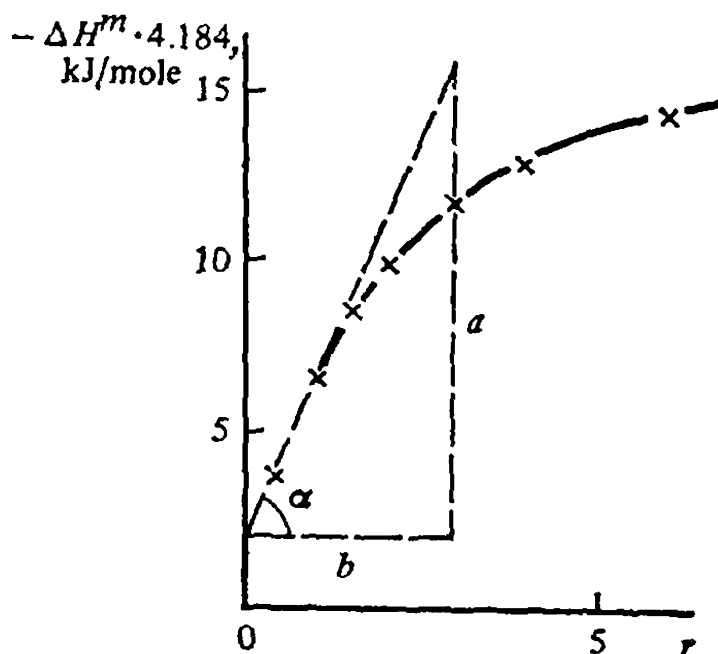


Fig. 16. Integral heat of solution of H_2SO_4 in water versus molar ratio between water and acid

number of moles of the solvent varies. The value of ΔH^m corresponds to the heat of formation of a solution containing one mole of H_2SO_4 and r moles of water. Therefore, it is advisable to plot, without resorting to additional conversions, ΔH^m as a function of r , to find $\Delta H_{\text{H}_2\text{O}}^m$ by the tangent method, and to calculate $\Delta H_{\text{H}_2\text{SO}_4}^m$ using the Gibbs-Duhem equation. Express the concentration of the 84.5% solution as the following molar ratio:

$$r = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{SO}_4}} = \frac{15.5 \times 98}{18 \times 84.5} = 1$$

Plot $\Delta H^m = f(r)$ (Fig. 16). Draw a line tangent to the curve at the point corresponding to $r = 1$. According to the equation $\Delta H_{\text{H}_2\text{O}}^m =$

$= \tan \alpha,$

$$\tan \alpha = \frac{a}{b} = \frac{13.56}{3} = 4.52$$
$$\Delta H_{\text{H}_2\text{O}}^m = \bar{Q}_{\text{H}_2\text{O}} = -18.92 \text{ kJ/mole}$$

To calculate $\bar{Q}_{\text{H}_2\text{SO}_4}$ use Eq. (12.15):

$$\Delta H^m = n_{\text{H}_2\text{O}} \bar{Q}_{\text{H}_2\text{O}} + n_{\text{H}_2\text{SO}_4} \bar{Q}_{\text{H}_2\text{SO}_4}$$

or

$$\Delta H^m = r \bar{Q}_{\text{H}_2\text{O}} + 1 \bar{Q}_{\text{H}_2\text{SO}_4}$$
$$27.8 = 1 (-18.92) + 1 (\bar{Q}_{\text{H}_2\text{SO}_4})$$
$$\bar{Q}_{\text{H}_2\text{SO}_4} = -8.897 \text{ kJ/mole}$$

9. Calculate the differential heats of solution of sulphuric acid and water for an 84.5% solution by the intercept method if the con-

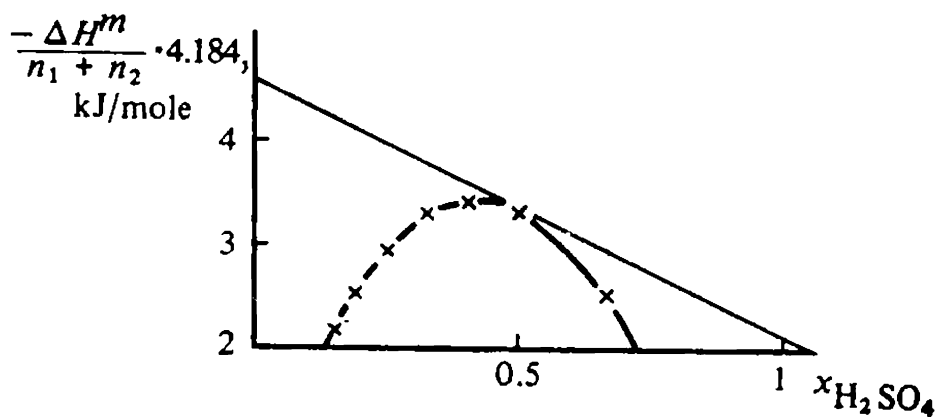


Fig. 17. Heat of solution of H_2SO_4 in water versus molar fraction of solution
centration dependence of the integral heat of solution at 298 K is given by the following values:

$r_1 = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{SO}_4}}$	0	0.5	1	1.5	2	3	4	6
$-\Delta H^m, \text{ kJ/mole}$	0	15.73	27.8	35.9	41.45	48.92	53.89	60.23

Solution. When the intercept method is used, concentrations are expressed either as molar fractions x or as percentage w_i . The integral heat of solution is related to one mole of the solution, therefore r and ΔH^m are given in terms of $x_{\text{H}_2\text{SO}_4} = 1/(r + 1)$ and $\Delta H^m/(n_1 + n_2) = \Delta H^m x_{\text{H}_2\text{SO}_4}$. Tabulate the initial data and the calculation results as follows:

r	0.5	1	1.5	2	3	4	6
$x_{\text{H}_2\text{SO}_4}$	0.666	0.5	0.4	0.33	0.25	0.20	0.15
$-\Delta H^m, \text{ kJ/mole}$	15.73	27.8	35.9	41.45	48.92	53.89	60.23
$-\Delta H^m x_{\text{H}_2\text{SO}_4}, \text{ kJ/mole}$	10.47	13.89	13.93	13.80	12.23	10.82	9.03

Plot a curve in the coordinates $\frac{\Delta H^m}{n_1 + n_2} - x_{\text{H}_2\text{SO}_4}$ (Fig. 17). The molar ratio of the 84.5% solution is $r = 1$, and the molar fraction $x_{\text{H}_2\text{SO}_4}$ is 0.5. Draw a line tangent to the curve at the point corresponding to 0.5 on the abscissa. The intercept at the ordinate gives the values of the differential heats of solution: a —water; b —sulphuric acid; $\Delta H_{\text{H}_2\text{SO}_4}^m = -8.87$ kJ/mole, $\Delta H_{\text{H}_2\text{O}}^m = -18.91$ kJ/mole.

10. The volume of a solution as a function of its composition for the H_2O - NaCl system is given by the equation

$$V_{\text{total}} = 55.55V_{\text{H}_2\text{O}} + 16.4m + 2.5m^2 - 1.2m^3$$

in which m is the molality of the solute. Determine the partial and apparent molar volumes of 0.5 M NaCl .

Solution. Differentiate the initial equation to derive the following equation for the partial molar volume:

$$\frac{\partial V_{\text{total}}}{\partial m} = \bar{V}_2 = 16.4 + 5m - 3.6m^2$$

Since $m = 0.5$, then $\bar{V}_2 = 18.0$. Determine the apparent molar volume at $m = 0.5$ using Eq. (12.19):

$$\varphi_{L_2} = \frac{L_{\text{total}} - n_1 L_1^0}{n_2}$$

Use the equation given in the statement of the problem to calculate $V_{\text{total}} = 1008.675$. Substitution of this value into Eq. (12.19) gives

$$\varphi_{V_2} = \frac{1008.675 - 55.55 \times 18}{0.5} = 17.35$$

11. Determine the partial molar heat capacities of HCl and H_2O in solutions characterized by the following molar fractions and heat capacities:

x_{HCl}	0.000	0.091	0.130	0.200	0.259
Heat capacity of a solution containing 1 M H_2O , J/K	75.3	70.9	69.5	72.7	82.6

Solution. First determine the partial molar heat capacities of the second component (HCl) because the above heat capacities relate to solutions containing a constant amount of the first component (H_2O). Thus, the quantities of interest will be the derivatives $\left(\frac{\partial C}{\partial n_2}\right)_{P, T, n_1}$ for all solutions. Each of these derivatives can be obtained

graphically (Fig. 18) as the slope of the line tangent to the curve representing C as a function of n_2 . Calculate the values of n_2 , which are necessary for plotting the curve, for all solutions using the fol-

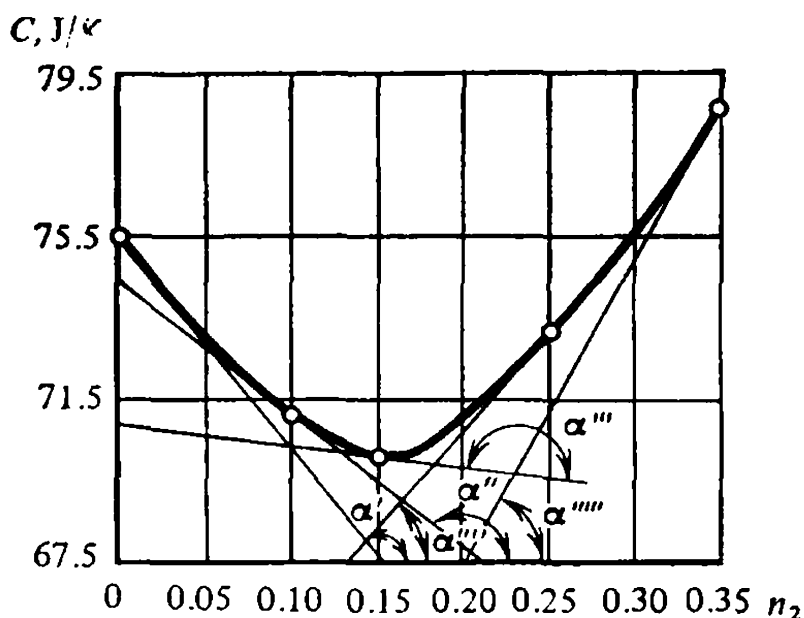


Fig. 18. Heat capacity of aqueous HCl solution versus HCl content in the solution

lowing expression for the molar fraction:

$$x_2 = \frac{n_2}{n_1 + n_2}$$

Since $n_1 = 1$, we have $n_2 = x_2/x_1$, and $n_2' = 0.0$

$$n_2'' = \frac{0.091}{0.909} = 0.1, \quad n_2''' = \frac{0.130}{0.870} = 0.149, \quad n_2'''' = \frac{0.200}{0.800} = 0.250$$

$$n_2''''' = \frac{0.259}{0.741} = 0.350$$

Use the plot to determine the derivatives corresponding to the partial molal heat capacities of HCl:

$$\bar{C}_2' = -12.9, \quad \bar{C}_2'' = -8.2, \quad \bar{C}_2''' = -1.5, \quad C_2'''' = 11.5, \quad C_2''''' = 18.6$$

To calculate the partial molar heat capacities of water use the equation

$$C = n_1 \bar{C}_1 + n_2 \bar{C}_2 \quad \text{or} \quad \bar{C}_1 = C - n_2 \bar{C}_2$$

$$C_1' = 18$$

$$C_1'' = 16.93 + 0.182 \times 0.1 = 17.75$$

$$C_1''' = 16.65 + 0.149 \times 1.5 = 16.87$$

$$C_1'''' = 17.36 - 0.25 \times 11.5 = 14.48$$

$$C_1''''' = 18.75 - 0.35 \times 18.6 = 12.24$$

12. Calculate the activity and rational activity coefficient of acetone in an aqueous solution of $x_{ac} = 0.318$, $P_{ac} = 152$ mm Hg, and $P_{ac}^\circ = 229$ mm Hg. Estimate the departure of the solution from ideal conditions.

Solution. To calculate the activity use Eq. (12.26):

$$a_{ac} = 152/229 = 0.664$$

Calculate the activity coefficient using Eq. (12.27):

$$\gamma_{ac} = 0.664/0.318 = 2.09$$

$\gamma_{ac} > 1$. The departures from Raoult's law are positive.

13. Calculate the chemical potential and its change during dissolution of acetone in water if $x_{ac} = 0.318$, $P_{ac} = 152$ mm Hg, and $P_{ac}^\circ = 229$ mm Hg. Find the necessary data in the handbook.

Solution. To calculate the change in chemical potential during dissolution we use Eq. (12.9):

$$\begin{aligned}\Delta\mu_{ac} &= \mu_{ac} - \mu_{ac}^\circ = RT \ln a_{ac} \\ &= 8.31 \times 2.3 \times 298 \log 0.664 = 1.013 \text{ kJ/mole}\end{aligned}$$

Since $\mu_{ac}^\circ = \Delta G_{ac}^\circ$, use Eq. (7.37) to calculate ΔG_{ac}° , the necessary data finding in the handbook. Accordingly, $\Delta G_{ac}^\circ = -155.50$ kJ/mole, and Eq. (12.9) gives

$$\mu_{ac} = -155.50 - 1.01 = -156.51 \text{ kJ/mole}$$

14. The temperature dependence of the saturated vapour pressure (Pa) of pure silver and silver over a solid Ag-Au solution with 30% mol. Ag is given by the equations:

$$\log P^\circ = -\frac{16\,350}{T} + 12.805$$

$$\log P = -\frac{15\,250}{T} + 11.118$$

Derive the equations for the temperature dependence of the relative chemical potential of silver in a 30% Ag-Au solution.

Solution. As follows from Eqs. (12.9), (12.26), and (12.28),

$$\Delta\mu_{Ag}^m = \mu_{Ag} - \mu_{Ag}^\circ, \quad \Delta\mu = RT2.3 \log P_{Ag} - RT2.3 \log P_{Ag}^\circ$$

Substitution of these values into the equation $\log P = f(T)$ gives

$$\mu_{Ag} - \mu_{Ag}^\circ = RT2.3 \left(-\frac{15\,250}{T} + 11.118 + \frac{16\,350}{T} - 12.805 \right)$$

$$R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}, \quad \text{and} \quad \mu_{Ag} - \mu_{Ag}^\circ = 21\,024 - 32.26T$$

15. Calculate the relative partial molar entropy of silver (ΔS_{Ag}^m) for an Ag-Au solution with 30% mol. Ag if the temperature dependence of the saturated vapour pressure (Pa) of pure silver and silver

over the solid solution is given by the equations:

$$\log P^\circ = -\frac{16\,350}{T} + 12.805$$

$$\log P = -\frac{15\,250}{T} + 11.118$$

Solution. To determine the partial molar entropy of silver use the equation

$$\Delta S_{\text{Ag}}^m = \left(-\frac{\partial \Delta \mu_{\text{Ag}}}{\partial T} \right)_{P, x_{\text{Ag}}}$$

But first find the derivative $\left(\frac{\partial \Delta \mu}{\partial T} \right)_{P, x_{\text{Ag}}}$ by differentiating the equation $\Delta \mu_{\text{Ag}} = f(T)$,

$$\left(\frac{\partial \Delta \mu}{\partial T} \right)_{P, x_{\text{Ag}}} = -32.26 \text{ J/mole}, \quad \Delta S_{\text{Ag}}^m = 32.26 \text{ J/mole}$$

16. Calculate the relative partial molar entropy of water ($\Delta S_{\text{H}_2\text{O}}^m$) for an 84.5% solution of sulphuric acid at 25 °C. The saturated water vapour pressures over water and over the solution are 3.167×10^3 and 5.198 Pa, respectively.

Solution. To calculate the relative partial molar entropy of water use Eq. (12.25). Use Eq. (12.26) to calculate its activity; $\Delta H_{\text{H}_2\text{O}}^m = -18.912 \text{ kJ/mole}$. Substitute the numbers into Eq. (12.25):

$$\Delta S_{\text{H}_2\text{O}}^m = -\frac{18.912}{298} - 2.3 \times 8.314 \log \frac{5.198}{3.167 \times 10^3} = -10.22 \text{ J mole}^{-1} \text{ K}^{-1}$$

17. Calculate the heat of solution (q_{sol}) of 40 g H_2SO_4 in 160 g H_2O . Use the concentration dependence of the integral heats from the handbook.

Solution. The dissolution can be written as



To calculate the heat of solution use Eq. (12.31): $q_{\text{sol}} = \Delta H^m n_2$ (the heats of solution of pure substances equal zero), where ΔH^m is the integral heat of solution, related to one mole of sulphuric acid. Find the value of ΔH^m in the handbook. Since the concentrations are expressed in the handbook as molar ratios r , then

$$r = m_{\text{H}_2\text{O}} M_{\text{H}_2\text{SO}_4} / (M_{\text{H}_2\text{O}} m_{\text{H}_2\text{SO}_4}) = 160 \times 98 / (18 \times 40) = 21.77$$

Given the value of r , find the integral heat of solution in the handbook. It equals -71.71 kJ/mole . Next, determine the number of moles of H_2SO_4 :

$$n_2 = m_{\text{H}_2\text{SO}_4} / M = 40 / 98 = 0.408$$

and calculate q_{sol} :

$$q_{\text{sol}} = 0.408 (-71.71) = -29.25 \text{ kJ}$$

18. Determine the heat of dilution (q_{dil}) of a 30.8% NaOH solution to 0.443%.

Solution. If the amounts of the solution are not stated in the problem, the calculation is based on one mole of the solute according to Eq. (12.31). The dilution process may be expressed as follows:



Then,

$$q_{\text{dil}} = \Delta H_2^m (\text{solution 2}) - \Delta H_1^m (\text{solution 1})$$

Convert the weight percentage of NaOH into molar ratios r . According to Eq. (12.2), $r = n_{\text{H}_2\text{O}}/n_{\text{NaOH}}$:

$$r_1 = \frac{69.2 \times 40}{18 \times 30.8} = 5, \quad r_2 = \frac{99.55 \times 40}{18 \times 0.443} = 500$$

and the integral heats of solution, ΔH_1^m and ΔH_2^m , can be found in the handbook: $\Delta H_1^m = -37.76 \text{ kJ/mole}$; $\Delta H_2^m = -42.36 \text{ kJ/mole}$. Calculate q_{dil} :

$$q_{\text{dil}} = -42.36 - (-37.76) = -4.6 \text{ kJ/mole}$$

19. Determine the heat of solution of 0.1 kg of gaseous hydrogen chloride at 298 K and $1.013 \times 10^5 \text{ Pa}$ in 3 kg of a 10% aqueous solution of HCl.

Solution. The dissolution process can be written as follows:



To calculate the heat of solution (q_{sol}) use Eq. (12.31):

$$q_{\text{sol}} = (n_1 + n_2) \Delta H_2^m - n_1 \Delta H_1^m$$

where n_1 is the number of moles of HCl in solution 1, and n_2 is the number of moles of gaseous HCl dissolved in the 10% aqueous solution of HCl.

Calculate $n_{\text{H}_2\text{O}}$, n_1 , and n_2 :

$$n_{\text{H}_2\text{O}} = \frac{3000 \times .09}{18} = 150, \quad n_1 = \frac{3000 \times 0.1}{36.5} = 8.219$$

$$n_2 = \frac{100}{36.5} = 2.739$$

Express the solution concentrations in terms of molar ratios r_1 and r_2 :

$$r_1 = \frac{n_{\text{H}_2\text{O}}}{n_1} = \frac{250}{8.219} = 18.26, \quad r_2 = \frac{n_{\text{H}_2\text{O}}}{n_1 + n_2} = \frac{150}{8.219 + 2.739} = 13.69$$

Find the integral heats of solution in the handbook, then linear interpolation (graphical interpolation is preferable in calculations requiring a high degree of accuracy) gives

$$\Delta H_1^m = -71.6, \quad \Delta H_2^m = -70.6 \text{ kJ/mole}$$

Calculate q_{sol} :

$$q_{\text{sol}} = (8.219 + 2.739)(-70.6) - 8.219(-71.6) = -185.2 \text{ kJ}$$

Problems

1. $1 \times 10^{-3} \text{ m}^3$ of sodium bromide contains 0.3219 kg NaBr. The density of the solution at 293 K is 1238.2 kg/m^3 . Express the concentration of the solution in terms of: (1) moles of the salt in $1 \times 10^{-3} \text{ m}^3$ of the solution, (2) moles of the salt per kg of water, (3) molar fractions, (4) percentage, and (5) moles of water per mole of NaBr.

2. The density of a 60% solution of orthophosphoric acid at 293 K is 1426 kg/m^3 . Determine the number of moles of H_3PO_4 (1) in one litre of the solution and (2) per 1000 g of the solvent. What is the molar fraction of the acid in the solution?

3. The density of a 5.18% aqueous solution of phenol is 1.0042 g/cm^3 . The density of water is 0.9991 g/cm^3 . Express the composition of the solution in terms of moles of phenol per mole of water and moles of phenol per litre of the solution. What is the specific volume of phenol in the solution if it is assumed that the specific volume of water remains invariable throughout the formation of the solution?

4. At 80°C the density of a 12% aqueous solution of phenol is 0.9775 g/cm^3 . What is the quantity of water per mole of phenol? What is the specific volume of phenol if that of water is $1.029 \text{ cm}^3/\text{g}$ and the solution is formed without any change in volume?

5. The density of CS_2 at 293 K is 1.264 g/cm^3 , and that of $\text{C}_2\text{H}_5\text{OH}$ is 0.8040 g/cm^3 . What is the density of mixture containing 80% CS_2 if its specific volume is an additive function of composition?

6. The density of a 10% solution of NH_4Cl is 1.029 g/cm^3 , the density of solid NH_4Cl is 1.536 g/cm^3 , and that of water is 0.9974 g/cm^3 . Find the change in volume when 100 g of a 10% solution are formed.

7. At 283 K the density of $\text{C}_2\text{H}_5\text{OH}$ is 0.7936 g/cm^3 , the density of water is 0.9991 g/cm^3 , and that of a 50% aqueous solution of the alcohol is 0.9179 g/cm^3 . Determine the amount of compression during mixing of 50 g of the alcohol with 50 g of water if the specific volume of the latter remains unchanged during the mixing. Compare the specific volume of pure alcohol with its specific volume in solution.

8. Determine graphically the partial molar volume of a 0.4 *m* solution of FeCl_3 proceeding from the following data:

Number of moles of FeCl_3 in 100 g of water	0.0000	0.0126	0.0257	0.0394	0.0536
Volume of the solution containing 100 g of water, cm^3	100.13	100.58	100.98	101.38	101.73

9. Determine graphically the partial molar volume of a 0.3 *m* solution of CuSO_4 proceeding from the following data:

CuSO_4 in solution, %	1.912	3.187	4.462	5.737
Solution density, g/cm^3	1.0190	1.0319	1.0450	1.0582

10. The relationship between the specific volume v of an aqueous solution of hydrogen peroxide and the weight percentage w of H_2O_2 is

$$v = 1.003 (1 - w) + 0.6935w - 0.036w (1 - w)$$

Calculate the partial molar volumes of H_2O and H_2O_2 for a solution in which $w = 0.4$.

11. Determine the partial molar volume of methanol if the density of its 60% aqueous solution at 293 K is 0.8946 g/cm^3 and the partial molar volume of water in the same solution is $16.8 \text{ cm}^3/\text{mole}$.

12. Determine the molar volume of a 20% aqueous solution of methanol if the partial molar volumes of water and alcohol in it are 18 and $37.8 \text{ cm}^3/\text{mole}$, respectively.

13. Determine the weight of one mole of a solution resulting from mixing one mole of CCl_4 with three moles of SnCl_4 .

14. Determine the molar volume of an alloy containing 62% Cu, assuming that the volume is an additive function of composition. The density of copper is 8.9 g/cm^3 , and that of zinc is 7.1 g/cm^3 .

15. The relationship between the volume of a sodium chloride solution and the number n_2 of moles of the salt dissolved in 1000 g of water is

$$V = 1000 + 16.4n_2 + 2.5n_2^2 - 1.2n_2^3$$

Determine the partial molar volume of 0.5 *m* of the NaCl solution (cm^3).

16. Determine the density of a 40% aqueous solution of methanol if the partial molar volumes of water and the alcohol in it are 17.5 and 39 cm³, respectively.

17. Determine the partial molar heat capacity of KOH in 10%, 20%, and 30% solutions, proceeding from the following data:

Number of moles of KOH in 100 g of water	Specific heat of the KOH solution, J g ⁻¹ K ⁻¹	Number of moles of KOH in 100 g of water	Specific heat of the KOH solution, J g ⁻¹ K ⁻¹
0.0000	4.176	0.5951	3.235
0.0940	3.896	0.7652	3.100
0.1985	3.699	0.9636	3.001
0.3152	3.524	1.1910	2.905
0.4465	3.337		

18. Determine the partial molar heat capacities of HNO₃ and H₂O in 0.5, 1.0, and 2.0 *m* solutions. The specific heat capacities of the nitric acid solutions are as follows:

x_{HNO_3} , %	0	1	2.5	5	10	15	20	25
Specific heat capacity, J g ⁻¹ K ⁻¹	4.18	4.117	4.034	3.908	3.712	3.545	3.373	3.219

19. At 298 K, the integral heat of solution of an acid in water is given by the equation

$$\Delta H = 8.35n_1^{1/2} + 12.54n_1^{3/2} + 16.72n_1^{5/2}$$

where n_1 is the number of moles of H₂O per mole of the acid. Determine $\Delta \bar{H}_2$ (i.e. $\partial \Delta H / \partial n_2$)_{P,T,n₁}) of a solution whose molar content is 10% acid.

20. Given the integral heats of solution of NaCl in water at 275 K:

Number of moles per kg of H ₂ O	0.0624	0.2001	0.4003	0.7504	1.0058
ΔH , J/mole	7716.3	7440.4	6897.0	6399.6	6015.0
Number of moles per kg of H ₂ O	1.9457	3.1064	4.0012	4.9966	6.0004
ΔH , J/mole	4961.7	3954.3	3206.1	2587.4	1897.7

calculate the amount of heat to be absorbed at this temperature after addition of 126 g H₂O to 100 g of the 10% aqueous solution of NaCl.

21. Given the integral and differential heats of solution of one mole of sulphuric acid in water at 298 K:

Number of moles, H ₂ O	ΔH , J	$\Delta \bar{H}_{\text{H}_2\text{O}}$, J/mole	$\Delta \bar{H}_{\text{H}_2\text{SO}_4}$, J/mole
0	0	-28 215.0	0
0.5	-15 925.8	-28 173.2	-1 830.8
1	-28 507.6	-19 771.4	-8 736.2
2	-41 632.8	-9 697.6	-22 237.6
3	-49 700.2	-6 186.4	-22 781.0
4	-54 841.6	-4 347.2	-37 452.8
6	-61 613.2	-2 382.6	-47 317.6
10	-67 883.2	-973.9	-58 143.8

determine (a) the total amount of the heat released when 4 moles of H₂O are added to a solution containing 6 moles of H₂O and one mole of H₂SO₄, and (b) the total amount of heat released when 3 moles of H₂O are mixed with 6 moles of H₂SO₄.

22. The following results have been obtained in studying the solubility of nickel dimethylglyoxime in water at several temperatures:

T, K	298	303	308	313	318
Solubility $\times 10^{-5}$, mole/litre	$0.105 \pm 9\%$	$0.139 \pm 4\%$	$0.184 \pm 2\%$	$0.240 \pm 2\%$	$0.307 \pm 2\%$

(a) determine the enthalpy of solution of nickel dimethylglyoxime in water, ΔH° (kJ/mole), and (b) explain the meaning of the superscript "o" in ΔH° .

23. Given the relationship between the heat of mixing of copper with silver and the composition at 1428 K, determine graphically the heats of solution of the components in solutions of the following composition: $x_{\text{Ag}} = 0.10, 0.30, 0.50, 0.70$, and 0.90 . Plot the heat of solution versus composition if

x_{Ag}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
ΔH , kJ/mole	1.38	2.41	3.14	3.60	3.81	3.77	3.46	2.81	1.78

24. When 125.4 g of bismuth are mixed with 9.73 g of magnesium, 16 200 J of heat are released. Determine the partial molar heat of solution of bismuth if that of magnesium in this solution is -34 900 J/mole.

25. The partial molar heats of solution of silicon and manganese in a Si-Mn solution in which the molar content of silicon is 70% are -3800 and -83 500 J/mole, respectively. Determine the amount

of heat released during formation of 1 kg of the solution of the above composition.

26. The partial molar entropy of solution of silver in solid Au-Ag solutions depends on composition and is given by the equation

$$\Delta \bar{S}_{\text{Ag}} = -R \ln x_{\text{Ag}} - 5.03x_{\text{Au}}^2 \text{ J mole}^{-1} \text{ K}^{-1}$$

Derive the dependence of ΔS^m on composition and calculate ΔS^m for a 75% solution of gold.

27. The dependence of the partial molar heat and entropy of solution of γ -Fe on the composition of the γ -Fe-Ni solution is given by the equations

$$\Delta H_{\gamma\text{-Fe}} = -2095x_{\text{Ni}}^2 \text{ J/mole}, \quad \Delta S_{\gamma\text{-Fe}} = -R \ln x_{\gamma\text{-Fe}}$$

Determine the dependence of the chemical potentials on the composition of the solution.

28. Calculate the activity of water in a solution if the water vapour pressure over the latter is $0.9333 \times 10^5 \text{ Pa}$ at 373 K.

29. At 308 K, the acetone vapour pressure is $0.459 \times 10^5 \text{ Pa}$ and the chloroform vapour pressure is $0.391 \times 10^5 \text{ Pa}$. The partial acetone vapour pressure over a solution in which the molar content of chloroform is 36% equals $0.2677 \times 10^5 \text{ Pa}$, and the partial chloroform vapour pressure over the same solution is $0.0964 \times 10^5 \text{ Pa}$. Determine the activity of the solution components and compare it with the molar fractions of these substances.

30. Calculate the activity coefficient of bromine in a carbon tetrachloride solution over which the partial bromine vapour pressure is 10.27 mm Hg. The solution has the following composition (molar fractions): Br_2 0.0250 and CCl_4 0.9750. The pure bromine vapour pressure at the same temperature is 213 mm Hg. Assume that the standard state of bromine is that of a pure liquid.

31. If 1.046 g of cadmium are dissolved in 25.23 g of mercury, the pressure of the resulting amalgam vapour at 305.2 K will be 0.920 of the pure mercury pressure. Determine the activity and the activity coefficient (molar fractions) of mercury in the amalgam.

32. Mercury chloride, Hg_2Cl_2 , is distributed between benzene and water; the following concentrations have been achieved at 298 K (mole/litre):

in C_6H_6	0.000155	0.000310	0.000618	0.00524	0.0210
in H_2O	0.001845	0.00369	0.00738	0.0648	0.2866

Calculate the activity of the salt in an aqueous solution where its concentration is 0.2866 mole/litre if its solution in benzene remains ideal up to $c = 0.03 \text{ mole/litre}$.

33. Determine the activity coefficient of sugar in a solution if the freezing point of its 0.8 *m* aqueous solution is 271.4 K. The cryoscopic constant of water is 1.86.

34. The temperature dependence of the vapour pressure (Pa) over liquid *n*-butane at temperatures ranging from 272.66 to 348.16 K is given by the equation

$$\log P = 0.813 - \frac{203.8}{T - 22.2} \left(\log P = 4.11 - \frac{1030.3}{251.0 + t} \text{ atm} \right)$$

Calculate the volatility of *n*-butane at 289.16 K if the density of its saturated vapour at this temperature is 4.9 kg/m³. Can the difference between volatility and the saturated vapour pressure be ignored if the expected accuracy of calculation using the above equation is about 1%?

35. Determine the volatility of NH₃ under conditions when one mole of NH₃ occupies a volume of 0.7696 litre at 4.05×10^6 Pa and 423 K.

36. The water vapour pressure at 293 K is 2337.80 Pa. Calculate the vapour pressure of a solution of 1×10^{-2} kg of ammonium chloride in 1×10^{-1} kg of water and the chemical potential of water in this solution if the activity coefficient γ of water is 0.976, assuming that ΔG° of water in the range of 293 to 298 K is independent of temperature and $\mu^\circ = \Delta G^\circ$ of formation of the component in question.

37. The water vapour pressure at 273 K is 610.48 Pa, and the vapour pressure of a 10% solution of NaNO₃ is 589.28 Pa. Determine the activity and chemical potential of water in this solution.

38. The bromine vapour pressure over pure bromine at 298 K is 28 371.00 Pa, while that in a 0.1 *m* aqueous solution is 1.7×10^4 Pa. Determine the chemical potential of bromine at 298 K. Assume that the standard state of bromine is that of a pure liquid.

39. Mercury chloride, Hg₂Cl₂, is distributed between benzene and water at 298 K in the following concentrations (mole/litre):

in C ₆ H ₆	0.000155	0.000310	0.000618	0.00524	0.0210
in H ₂ O	0.001845	0.00369	0.00738	0.0648	0.2866

Calculate the chemical potential μ in both phases as a function of concentration and plot the corresponding curve.

40. At 1250 K, the saturated silver vapour pressure over an Ag-Au solution in which the molar content of silver is 62.0% as well as over pure silver is 2.11×10^{-1} and 4.83×10^{-1} Pa, respectively. Determine the relative chemical potential of silver in the solution.

41. The saturated vapour pressures over pure lead, silver, and an Ag-Pb solution in which the molar content of silver is 95% at 1358 K are as follows: $P_{\text{Ag}}^\circ = 8.67 \times 10^{-1}$ Pa, $P_{\text{Ag}} = 8.40 \times 10^{-1}$ Pa, $P_{\text{Pb}}^\circ = 5.59 \times 10^2$ Pa, and $P_{\text{Pb}} = 9.60 \times 10$ Pa.

Determine the change in Gibbs' energy per mole of the solution of a given composition.

42. The temperature dependence of the saturated vapour pressure (Pa) of pure liquid copper is given by the equation

$$\log P^\circ = -16\,050/T + 10.666$$

Determine the partial molar heat of solution of copper at 1823 K in a Fe-Cu solution (the copper concentration being 89.5%) if the saturated vapour pressure of copper over this solution is 6.73×10^1 Pa.

43. The saturated vapour pressure (Pa) of magnesium over a Mg-Pb solution containing 4.2% Mg is temperature-dependent according to the equation

$$\log P = -\frac{7810}{T} + 9.218$$

The similar equation for the saturated vapour pressure over pure magnesium is

$$\log P^\circ = -\frac{6560}{T} + 9.723$$

Determine the partial molar heat and entropy of solution of magnesium at 298 K.

44. The gas phase $\text{H}_2\text{O}-\text{H}_2$ which is at equilibrium, at 1873 K, with a solution of oxygen in iron (the oxygen content by volume is 0.1200%) contains 72.1% H_2 . Determine the change in the chemical potential of oxygen during transition from the gas phase in which $P_{\text{O}_2} = 10^5$ Pa into solution of the above composition. The equilibrium constant of the reaction $\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O}$ at 1873 K is

$$K_P = P_{\text{H}_2\text{O}}/P_{\text{H}_2}P_{\text{O}_2}^{1/2} = 9.46 \times 10^3$$

45. 400 g of water are mixed with 100 g of 100% H_2SO_4 . The evolving heat is expended in heating the solution. Calculate the change in the solution temperature (ΔT) assuming that the vessel containing the solution does not absorb heat. The heat capacity of the solution is constant and equal to $3.427 \text{ J g}^{-1} \text{ K}^{-1}$. Find the necessary data in the handbook.

Multivariate Problems

1. The density of a solution of substances A and B in given concentrations is d at temperature T : (1) determine the molar concentration or, in other words, the number of moles of the solute per litre of the solution; (2) determine the molality or, in other words, the number of moles of the solute per kg of the solvent; (3) calculate the mole percentage of substance A; and (4) determine the number of moles of the solvent per mole of the solute.

Variant	Weight percentage of A	Substance		T, K	$d \times 10^{-3}$, kg/m ³
		A	B		
1	97	CBr ₃ CHO	H ₂ O	323	2.628
2	94	CBr ₃ CHO	H ₂ O	313	2.566
3	91	CBr ₃ CHO	H ₂ O	313	2.485
4	87	CBr ₃ CHO	H ₂ O	313	2.340
5	80	CBr ₃ CHO	H ₂ O	313	2.106
6	73	CBr ₃ CHO	H ₂ O	313	1.938
7	63	CBr ₃ CHO	H ₂ O	313	1.725
8	45	CBr ₃ CHO	H ₂ O	313	1.476
9	72	C ₆ H ₅ (SO ₃ H)	H ₂ O	298	1.281
10	66	C ₆ H ₅ (SO ₃ H)	H ₂ O	298	1.256
11	61	C ₆ H ₅ (SO ₃ H)	H ₂ O	298	1.235
12	80	C ₆ H ₃ (OH) ₃	H ₂ O	293	1.208
13	62	(CH ₂) ₄ O ₂	H ₂ O	293	1.041
14	57	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.992
15	50	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.968
16	43	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.945
17	37	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.921
18	30	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.900
19	28	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.875
20	17	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.850
21	12	C ₁₀ H ₈	CH ₃ COCH ₃	293	0.835
22	80	C ₆ H ₁₄	CH ₃ COCH ₃	293	0.765
23	60	C ₆ H ₁₄	CH ₃ COCH ₃	293	0.741
24	40	C ₆ H ₁₄	CH ₃ COCH ₃	293	0.719
25	20	C ₆ H ₁₄	CH ₃ COCH ₃	293	0.692

2. Given the relationship between the integral heats of mixing, ΔH_{mix} , and the concentration in the liquid phase, x_i^{liq} , at 298 K and 1.0133×10^5 Pa, as well as the vapour composition, x_i^v , and the total pressure at T , K: (1) plot the $\Delta H_{mix} = f(x_i^{liq})$ curve; (2) determine the integral heat of the mixing of the components for 1 g of the mixture; (3) determine, using all possible methods, the partial heats of mixing of the i th component at concentrations m_i and x_i^{liq} ; (4) determine the apparent molar heat of mixing of the i th component at concentration x_i^{liq} ; (5) determine the partial pressure of the i th component for the tabulated mixtures; (6) calculate the activity of the i th component for the tabulated mixtures; (7) determine the relative chemical potential of the i th component for the tabulated mixtures; (8) determine the activity coefficient of the i th

Variant	Mole per-centage of the 1st component, x_1^{liq}	Molality of the solution	Mole per-centage of the 1st component in vapours, x_1^v	Saturated vapour pressure over the mixture, mm Hg	System A-B	Mole per-centage of 2nd component, x_2^{liq}	Heat of mixing per mole of the mixture for A-B system, J
1	3.32	0.1	7.98	146.7	CCl ₄ (1)-C ₇ H ₁₆ (2) ($T=323$ K, $P_{C_7H_{16}}^\circ=140.5$ mm Hg, $P_{CCl_4}^\circ=308.5$ mm Hg)	0	0
2	96.49		99.14	304.1		0.1	-110.876
	9.83	0.15	21.59	159.8		0.2	-200.832
3	89.92		94.68	295.4		0.3	-277.399
	17.14	0.2	34.37	174.0		0.4	-327.189
4	81.26		90.00	282.4		0.5	-347.272
	30.24	0.3	52.79	198.7		0.6	-326.352
5	73.23		85.54	271.4		0.7	-271.960
	35.69	0.5	58.05	207.4		0.8	-194.556
6	64.96		80.53	256.9		0.9	-100.416
	43.24	0.4	64.52	220.7		0	0
7	57.00		75.15	244.7			
	50.12	0.6	70.00	232.3			
8	73.23		85.54	271.1			
	9.83	0.7	21.59	159.8			
	64.96		80.53	256.9			
9	17.14		38.37	174.0			
	96.49	0.8	99.14	304.1			
	3.32		7.98	146.7			
10	57.00	0.5	75.15	244.7			
11	6.84	0.1	45.56	103.6	C ₂ H ₅ OH(1)-C ₇ H ₁₆ (2) ($T=303$ K, $P_{C_7H_{16}}^\circ=58.2$ mm Hg,	0	0
	71.74		58.28	119.6		0.1	-259.400
12	28.03	0.2	53.44	117.7		0.2	-401.664

13	51.51 28.03 81.54 6.84 89.02 51.51 95.45 6.84 71.74	0.3 0.4 0.5 0.6	54.96 58.28 62.82 45.56 71.16 54.96 89.68 45.56 58.28	119.9 119.6 117.0 103.6 111.3 119.9 97.1 103.6 119.6	$P_{C_2H_5OH}^\circ = 78.2 \text{ mm Hg}$	0.3 0.4 0.5 0.6 0.7	-512.958 -595.801 -633.876 -614.211 -560.656
17	10	0.2	16.48	156.0	$C_2H_5OH(1)-C_6H_{14}(2)$ ($T = 298 \text{ K}$, $P_{C_6H_{14}}^\circ = 140.3 \text{ mm Hg}$, $P_{C_2H_5OH}^\circ = 78.2 \text{ mm Hg}$)	0	0
18	90	0.3	36.69	109.3		0.1	-255.224
19	20	0.1	20.90	158.4		0.2	-380.744
20	80	0.7	27.40	138.3		0.3	-460.240
21	30	0.8	22.08	157.6		0.4	-517.142
22	70	0.9	24.47	150.0		0.5	-558.146
23	40	1.1	22.46	157.2		0.6	-566.000
24	10	1.2	36.69	109.3		0.7	-556.472
25	50	1.3	22.83	156.4		0.8	-510.448
	90		36.69	109.3			
	60		23.21	154.7			
	20		20.90	158.4			
	70		24.47	150.0			
	30		22.08	157.6			
	80		27.40	138.3			
	10		16.48	156.0			
	90		36.69	109.3			
	20		20.90	158.4			
	80		27.40	138.3			
	10		16.48	156.0			
	90		36.69	109.3			
	20		20.90	158.4			

component for the tabulated mixtures; and (9) determine the entropy of mixing at the tabulated concentrations, assuming that the heat of mixing is independent of temperature.

In each variant, the calculations should be performed for two compositions.

CHAPTER 13

Dilute Solutions

Basic Equations and Symbols

The relative pressure of saturated vapours over a solution of solid substances in volatile solvents is given by Raoult's law (relative decrease in the solvent vapour pressure over the solution):

$$\frac{P_i^\circ - P_i}{P_i^\circ} = \frac{\Delta P}{P_i^\circ} = \frac{n_2}{n_1 + n_2} = x_2 \quad (13.1)$$

where P_i° is the vapour pressure over the pure solvent, P_i is the solvent vapour pressure over the solution of a given concentration, $\Delta P/P_i^\circ$ is the relative decrease in the solvent vapour pressure, n_2 is the number of moles of the solute, and n_1 is the number of moles of the solvent.

When the dissociation (association) of the solute is taken into account, Raoult's equation takes the form

$$\frac{\Delta P}{P_i^\circ} = \frac{in_2}{n_1 + n_2} \approx \frac{in_2}{n_1} \quad (13.2)$$

where i is the van't Hoff factor:

$$i = \frac{\text{total number of moles with dissociation}}{\text{total number of moles without dissociation}} = 1 + \alpha(v - 1) \quad (13.3)$$

where α is the degree of dissociation = $\frac{\text{number of dissociated molecules}}{\text{initial number of molecules}}$, and v is the number of the particles into which the molecule dissociates.

The increase in the boiling point ($\Delta T_b = T - T^\circ$) of a dilute solution relates to the molality m as follows in the case of non-dissociating substances:

$$\Delta T_b = K_e m \quad (13.4)$$

and for dissociating substances the relation is

$$\Delta T_b = i K_e m \quad (13.5)$$

where T° and T stand for the boiling points of the solvent and solution, respectively, and K_e is the ebullioscopic constant (molar elevation in the boiling point);

$$K_e = \frac{RT_{n.b.}^2}{1000l_{\text{evap}}} \quad (13.6)$$

where $T_{n.b.}$ is the normal boiling point of the pure solvent, and l_{evap} is the specific heat of evaporation of the solvent.

The elevation in the boiling point of a solution is instrumental in determining the molecular weight of the solute:

$$M_2 = \frac{1000K_em_2}{m_1\Delta T_{\text{evap}}} \quad (13.7)$$

where M_2 is the molecular weight of the solute, m_2 is the mass of the solute, and m_1 is that of the solvent.

The depression in the freezing point ($\Delta T_f = T_f^\circ - T$) of a dilute solution relates to the molality m as follows for non-dissociating substances:

$$\Delta T_f = K_{cr}m \quad (13.8)$$

while in the case of dissociating substances the relation is

$$\Delta T_f = iK_{cr}m \quad (13.9)$$

where K_{cr} is the cryoscopic constant of the solvent (molar depression in the freezing point);

$$K_{cr} = \frac{RT_m^2}{1000l_{fus}} \quad (13.10)$$

T_f° and T stand for the freezing points of the pure solvent and solution, respectively, and l is the specific heat of fusion of the solvent.

The depression in the freezing point of a solution allows one to determine the molecular weight of the solute:

$$M_2 = \frac{1000K_{cr}m_2}{m_1\Delta T_f} \quad (13.11)$$

The relationship between osmotic pressure and the molarity (van't Hoff's relation) is

$$\pi = cRT \quad (13.12)$$

for non-dissociating substances and

$$\pi = icRT \quad (13.12a)$$

for dissociating ones, π being osmotic pressure and c being the solution concentration in mole/litre.

The integral heat of solution, ΔH^m , for dilute solutions is given by the equation

$$\Delta H^m = n_2 \Delta H_2^m \quad (13.13)$$

The chemical potential of the components of a finitely dilute solution takes the form of the following equations:

$$\mu_1 = \mu_1^0 + RT \ln x_1 \quad (13.14)$$

$$\mu_2 = \mu_2^* + RT \ln m \quad (13.15)$$

in which μ_2^* is the chemical potential of the second component in a hypothetical solution whose molality is $m = 1$ mole per 1000 g and which exhibits the properties of a finitely dilute solution.

The relationship between the solubility of gases in liquids and pressure is given by Henry's equation

$$x_2^{\text{liq}} = K_H P_2 \quad (13.16)$$

$$P_2 = K'_H x_2^{\text{liq}} \quad (13.17)$$

where x_2^{liq} is the gas concentration in a saturated solution, and K'_H and K_H are the Henry constants;

$$K'_H = 1/K_H$$

and P_2 is the partial gas pressure.

The temperature dependence of the solubility of a gas is expressed as the following differential equation:

$$\left(\frac{\partial \ln x_2}{\partial T} \right)_{P, \text{ sat. sol.}} = \frac{\Delta H_2^m}{RT^2} \quad (13.18)$$

or integral equation (for the temperature range in which ΔH_2^m is constant):

$$\ln \frac{(x_2)_{T_2}}{(x_2)_{T_1}} = -\frac{\Delta H_2^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (13.19)$$

where ΔH_2^m is the differential heat of solution of the gas in the saturated solution. Equations (13.16) and (13.18) are applicable to ideal and finitely dilute solutions.

For a given temperature, the ratio of the concentrations of a third component in two equilibrium phases is a constant quantity independent of the absolute amounts of all the substances involved in the distribution:

$$c_1/c_2 = K \quad (13.20)$$

where c_1 is the equilibrium concentration of the substance being distributed in the first phase, c_2 is that of the substance being distributed in the second phase, and K is the distribution number (or coefficient).

In some systems, the substance being distributed is characterized by dissimilar average numbers of particles in different solvents as a result of dissociation of its molecules. Then, Eq. (13.20) is no

more applicable, and the equation of the distribution law takes the form

$$c_1^n/c_2 = K \quad (13.21)$$

where $n = M''/M'$ (M' is the mean molecular weight of the substance being distributed in the first phase, and M'' is the mean molecular weight of the substance being distributed in the second phase). When a third substance is distributed between two immiscible liquids, it may so happen that the degree of dissociation of the distributing substance differs from one solvent to the other. Let the degree of dissociation of such a substance be α_1 in the first solvent, and α_2 in the second. Then the distribution law will be written as

$$c_1 (1 - \alpha_1)/[c_2 (1 - \alpha_2)] = K \quad (13.22)$$

To modify the distribution law (13.20) for concentrated solutions, activities should be substituted for concentrations:

$$a_1/a_2 = K \quad (13.23)$$

where a_1 and a_2 stand for the activities of the substance being distributed in the first and second phases, respectively. If the relationship between the activity and the concentration of the substance being distributed in one of the solvents is known along with the distribution coefficient, a similar relationship can be established for the conjugate solution.

The distribution law is widely used when a substance is extracted from a solution. Let m_0 stand for the initial quantity of the substance being extracted, V_1 for the solution volume containing this substance, V_2 for the solvent volume required for a single extraction, n for the total number of extractions, m_1, m_2, \dots, m_n for the quantity of the substance, remaining in the initial solution after the first, second, \dots , n th extractions, and K for the distribution coefficient of the substance being extracted. It is assumed that the latter coefficient is the ratio of the concentration of the solution from which the substance being distributed is extracted to that of the solution used for the extraction. Let m_1 kg of the dissolved substance remain in the volume V_1 after the first extraction and $m_e = m_0 - m_1$ kg be the actual extracted amount confined within the volume V_2 . According to the distribution law (13.20)

$$\frac{m_1/V_1}{(m_0 - m_1)/V_2} = K \quad (13.24)$$

hence,

$$m_1 = m_0 K V_1 / (K V_1 + V_2) \quad (13.25)$$

After the second extraction,

$$\frac{m_2/V_1}{(m_1 - m_2)/V_2} = K, \quad m_2 = m_1 \frac{K V_1}{K V_1 + V_2} \quad (13.26)$$

Simultaneous solution of Eqs. (13.25) and (13.26) gives

$$m_2 = m_0 \left(\frac{KV_1}{KV_1 + V_2} \right)^2 \quad (13.27)$$

After n extractions, the initial solution contains m kg of the dissolved substance:

$$m = m_0 \left(\frac{KV_1}{KV_1 + V_2} \right)^n \quad (13.28)$$

Exercises

1. The pressure of the water vapour of a solution containing a non-volatile solute is 2% below that of the vapour of pure water. Determine the molality of the solution.

Solution. Use the equation

$$(P_1^\circ - P_1)/P_1^\circ = x_2$$

Taking the pure solvent vapour pressure P_1° as 100 and P_1 as 98, we have

$$(100 - 98)/100 = 0.02 \quad \text{or} \quad x_2 = 0.02$$

To determine the molality m , calculate the number of moles of the solute per 1000 g of water, using the equation

$$x_2 = n_2/(n_2 + n_1)$$

in which n_1 is the number of moles of water and $n_2 = m$; $n_1 = 1000/18 = 55.56$. Substitution of these numbers into the equation gives

$$0.02 = m/(55.56 + m)$$

hence, $m = 1.134$.

2. What will be the change in the ratio between the vapour pressures over a solution and the solvent if the solute is dissociated by 80% into two ions and if the solute is not dissociated? The water vapour pressure of the solution containing a non-volatile solute is 2% below that of the pure water vapour.

Solution. Calculate the relative decrease in the pressure over the solution in which the substance undergoes dissociation and compare it with the relative decrease in pressure when no dissociation takes place. According to Eq. (13.2),

$$\frac{\Delta P}{P_1^\circ} = \frac{in_2}{x_1 + in_2}$$

$n_2 = m = 1.34$ moles per 1000 g; $n_1 = 55.55$.

Calculate i using Eq. (13.3):

$$i = 1 + 0.8(2 - 1) = 1.8$$

Substitution of the numbers gives

$$\left(\frac{\Delta P}{P_1^0}\right)_{\text{diss}} = \frac{1.8 \times 1.134}{55.55 + 1.8 \times 1.134} = 0.035$$

Find the ratio between the relative decreases in pressure with and without dissociation of the solute:

$$\left(\frac{\Delta P}{P_1^0}\right)_{\text{diss}} : \left(\frac{\Delta P'}{P^0}\right) = \frac{0.035}{0.02} = 1.75$$

3. Calculate the ebullioscopic constant K_e for water. The heat of evaporation ΔH_{evap} is 40.685 kJ/mole.

Solution. To calculate the ebullioscopic constant use Eq. (13.6):

$$K_e = \frac{RT_{\text{n.b.}}^2 M}{1000 \Delta H_{\text{evap}}} = \frac{8.314 (373.16)^2 \times 18}{1000 \times 40.685} = 0.512 \text{ deg/mole}$$

4. Determine the boiling point of an aqueous solution containing 0.01 mole of a non-volatile substance in 200 g of water.

Solution. Calculate T_b using Eq. (13.4):

$$K_e = 0.512 \text{ deg/mole}$$

Determine the molality of the solution:

$$m = 0.01 \times 5 = 0.05 \text{ mole per 1000 g of water}$$

Substitution of the numbers into Eq. (13.4) gives

$$\Delta T = 0.512 \times 0.05 = 0.0256$$

$$T = T^0 + \Delta T = 373.16 + 0.0256 = 373.186 \text{ K}$$

5. Calculate the molecular weight of a substance if the freezing point of a solution containing 100 g of benzene and 0.2 g of the substance of interest is 0.17 K below that of benzene. The cryoscopic constant K_{cr} is 5.16 deg/mole.

Solution. To calculate the molecular weight use Eq. (13.10):

$$M = 1000 \times 5.16 \times 0.2 / (100 \times 0.17) = 60.23$$

6. The decrease in the freezing point of an aqueous solution of a substance is 1.395 K, and that in the freezing point of a benzene solution of the same substance is 1.280 K. Why the difference in ΔT , if the molalities of the solutions are the same? What quantities representative of the state of the substance in the solution can be derived from the above data? K_{cr} is 5.16 deg/mole for benzene and 1.86 deg/mole for water.

Solution. The difference in freezing points can be explained by the fact that the substance dissociates in the aqueous solution but does not in the benzene one. Equations (13.8) and (13.9) can be used to calculate the van't Hoff factor i . Once the numerical value

of i is known, it is possible (using Eq. (13.3)) to infer the number ν of the particles into which the solute molecule dissociates, as well as the degree of dissociation α . According to the inferences made,

$$\Delta T_{\text{C}_6\text{H}_6} = 1.28 = 5.16m, \quad \Delta T_{\text{H}_2\text{O}} = 1.395 = i1.86m$$

$$\frac{\Delta T_{\text{H}_2\text{O}}}{\Delta T_{\text{C}_6\text{H}_6}} = \frac{1.395}{1.28} = \frac{i1.86}{5.16}, \quad t = \frac{5.16 \times 1.395}{1.28 \times 1.86} = 2.98$$

If the molecule yields two particles ($\nu = 2$) as it dissociates, then, even at $\alpha = 1$, $i = 2$. The resulting $i > 2$ indicates that $\nu > 2$. Calculate the degree of dissociation α using Eq. (13.3) and assuming that $\nu = 3$; then, $2.52 = 1 + \alpha(3 - 1)$ and, consequently, $\alpha = 0.76$. If $\nu = 4$, $\alpha = 0.50$, and so on.

7. A solution containing 0.8718 mole/litre of cane sugar at 291 K is isoosmotic with a solution of sodium chloride containing 0.5 mole/litre NaCl. Determine the apparent degree of dissociation and the van't Hoff factor for sodium chloride.

Solution. To determine the osmotic pressure for the sugar solution use the equation $\pi = c_1RT$ where c_1 is the sugar concentration in the solution. To do the same for the sodium chloride solution use the equation $\pi = ic_2RT$, in which c_2 is the NaCl concentration in the solution. Since the osmotic pressures of both solutions are equal, $c_1RT = ic_2RT$. Consequently,

$$i = c_1/c_2 \quad \text{or} \quad i = 0.8718/0.5 = 1.743$$

Using the equation $i = 1 + \alpha(\nu - 1)$, determine the apparent degree of dissociation. Since the sodium chloride molecule dissociates into two ions in solution, $\nu = 2$ and

$$\alpha = (1.743 - 1)/(2 - 1) = 0.743$$

8. Calculate the Henry constant K'_H for nitrogen at 298 K and 760 mm Hg. The Bunsen coefficient α is 0.0143 (which is the number of the nitrogen volumes, reduced to normal conditions, absorbed by one volume of water). The density of water is 0.997 g/cm³.

Solution. Calculate the number of moles of nitrogen absorbed by 1 cm³ of water, using Eq. (10.1):

$$n_{\text{N}_2} = \frac{1 \times 0.0143 \times 10^{-3}}{0.082 \times 273} = 6.38 \times 10^{-7} \text{ mole}$$

$$n_{\text{H}_2\text{O}} = \frac{1 \times 0.997}{18} = 0.0554 \text{ mole}$$

To calculate the molar fraction of nitrogen, x_{N_2} , use Eq. (13.3):

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{H}_2\text{O}} + n_{\text{N}_2}} = \frac{6.38 \times 10^{-7}}{5.54 \times 10^{-2}} = 1.15 \times 10^{-5}$$

Substitution of the pressure and concentration values into the equation gives K'_H :

$$K'_H = \frac{P_{N_2}}{x_{N_2}} = \frac{760}{1.15 \times 10^{-5}} = 6.61 \times 10^7$$

9. At 295 K and 51 987 Pa, the solubility of H_2 in aniline is 10.6 kg/m^3 , and at 154 628 Pa and the same temperature, it is 31.6 kg/m^3 . Is Henry's law applicable under these conditions?

Solution. If Henry's law is applicable, then the ratio of pressure to the equilibrium concentration of the gas in the liquid is a constant quantity proportional to the Henry constant K'_H . Calculate the pressure-to-concentration ratios:

$$51\,987/10.6 = 4904.4, \quad 154\,628/31.6 = 4893.3$$

Comparison of the results suggests that the answer is positive.

10. Calculate the heat of solution of nitrogen in water ($P_{N_2} = 760 \text{ mm Hg}$) proceeding from the temperature dependence of the Henry constant K'_H :

$T, \text{ K}$	273	283	293	303
$K'_H \times 10^{-7} \text{ mm Hg}$	4.02	5.08	6.12	7.02

Solution. Solve Eq. (13.17) for the molar fraction. Substitution of the result into Eq. (13.19) will give

$$\log \frac{P_{N_2}}{(K'_H)_{T_2}} - \log \frac{P_{N_2}}{(K'_H)_{T_1}} = \frac{\Delta H_2^m}{2.3R} \frac{T_2 - T_1}{T_2 T_1}$$

or

$$\log \frac{(K'_H)_{T_1}}{(K'_H)_{T_2}} = \frac{\Delta H_2^m}{2.3R} \frac{T_2 - T_1}{T_2 T_1}$$

Substitute the values of K'_H for the two temperatures into the equation:

$$\log \frac{4.02}{7.02} = - \frac{\Delta H_2^m}{2.3 \times 8.314} \frac{30}{273 \times 303}$$

and the result will be $\Delta H_2^m = 12.728 \text{ kJ/mole}$.

11. A 0.02 M aqueous solution of picric acid is at equilibrium with its 0.07 M solution in benzene. Calculate the coefficient of distribution of picric acid between benzene and water if its molecular weight is normal in the benzene solution, while in water picric acid undergoes partial dissociation, the degree of this dissociation being 0.9.

Solution. To determine the coefficient of distribution of picric acid between benzene and water divide its concentration in benzene by that of its undissociated portion in water:

$$K = 0.7/[0.02(1 - 0.9)] = 35$$

12. Distribution of salicylic acid between benzene and water at 298 K has resulted in the following concentrations:

c_1	0.0363	0.0668	0.0940	0.126	0.210
c_2	0.0184	0.0504	0.0977	0.146	0.329
c_1	0.283	0.558	0.756	0.912	
c_2	0.553	1.650	2.810	4.340	

where c_1 is the concentration of salicylic acid in the aqueous layer, mole/litre; and c_2 is the acid concentration in the benzene layer,

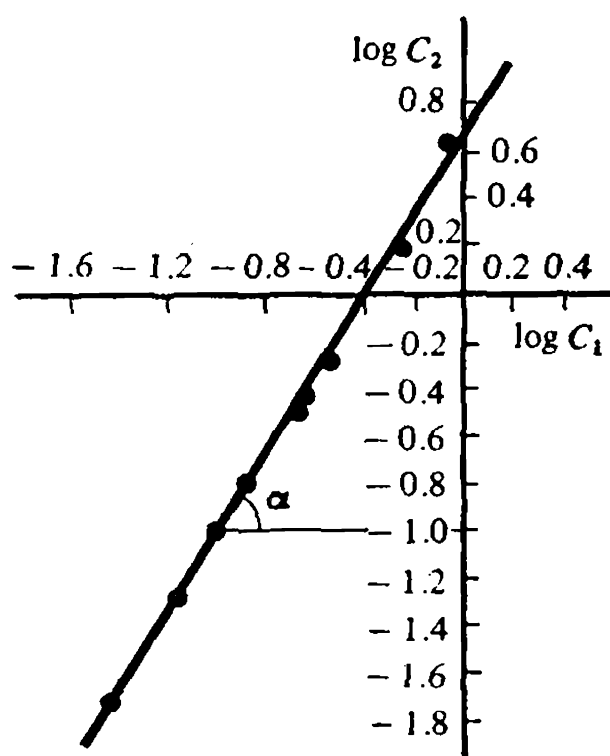


Fig. 19. Logarithm of concentration c_2 of a benzene solution of salicylic acid versus logarithm of concentration c_1 of an aqueous solution of the same acid

mole/litre. Plot the values of n and K and write the distribution equation.

Solution. Use Eq. (13.20) to calculate K ; $K = 1.97, 1.33, 0.96, 0.86, 0.64, 0.53, 0.34, 0.27$, and 0.21 . Since the c_1/c_2 ratio does not remain constant, changes in the molecular weight of the substance being distributed are observed. Apply the distribution law in its general form. Taking the logarithms of Eq. (13.21) gives

$$n \log c_1 - \log c_2 = \log K \quad \text{or} \quad \log c_2 = n \log c_1 - \log K$$

The latter is an equation for a straight line whose slope is n , and the intercept on the ordinate is $\log K$. Take the logarithms of the concentrations stated in the problem:

$\log c_1$	-1.4401	-1.1752	-1.0269	-0.8996	-0.6778
$\log c_2$	-1.7352	-1.2976	-1.0101	-0.8356	-0.4828
$\log c_1$	-0.5482	-0.2534	-0.1215	-0.0400	
$\log c_2$	-2.2733	+0.2175	+0.4487	+0.6375	

Use these data to plot $\log c_2$ versus $\log c_1$ (Fig. 19), and determine the slope of the straight line with respect to the abscissa:

$$\tan \alpha = \frac{1.66}{1.00} = 1.66, \quad n = 1.66 - \log K = 0.66$$

$$\log K = \bar{1}.34, \quad K = 0.219$$

For the system under consideration, the distribution law is given by the equation

$$c_1^{1.66}/c_2 = 0.219$$

13. The coefficient of distribution of iodine between water and carbon disulphide is 0.0017. An aqueous solution of iodine, containing 10^{-4} kg of iodine in 10^{-4} m³ of water, is shaken together with carbon disulphide. How much iodine will remain in the aqueous solution if 10^{-4} m³ of the latter is shaken with 5×10^{-6} m³ of carbon disulphide and if 10^{-4} m³ of the aqueous solution is shaken successively with five separate 10^{-6} m³ portions of carbon disulphide?

Solution. Determine the amount of iodine remaining after one extraction, with the aid of Eq. (13.25):

$$m_1 = 10^{-4} \frac{0.0017 \times 10^{-4}}{0.0017 \times 10^{-4} + 5 \times 10^{-6}} = 3.3 \times 10^{-6} \text{ kg}$$

The amount of extracted iodine will be

$$10^{-4} - 3.3 \times 10^{-6} = 0.967 \times 10^{-4} \text{ kg or } 96.7\%$$

Now determine the amount of iodine remaining after five extractions, with the aid of Eq. (13.28):

$$m_5 = m_0 \left(\frac{KV_1}{KV_1 + V_2} \right)^5$$

$$V_2 = 10^{-6} \text{ m}^3, \quad m_5 = 10^{-4} \left(\frac{0.0017 \times 10^{-4}}{0.0017 \times 10^{-4} + 10^{-6}} \right)^5 = 6.5 \times 10^{-9} \text{ kg}$$

The amount of iodine after five-fold extraction is

$$10^{-4} - 6.5 \times 10^{-9} = 0.999935 \times 10^{-4} \text{ kg or } 100\%$$

Problems

1. Determine the relative decrease in vapour pressure for a solution containing 0.01 mole of a non-volatile solute in 0.5 kg of water.

2. The water vapour pressure at 313 K is 7375.4 Pa. Calculate the vapour pressure, at the same temperature, of a solution containing 0.9206×10^{-2} kg of glycerol in 0.360 kg of water.

3. Calculate the ether vapour pressure over a 3% solution of aniline in ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, at 293 K. The ether vapour pressure at this temperature is 5.89×10^4 Pa.

4. The ethyl ether vapour pressure is 0.589×10^5 Pa at 293 K, and the vapour pressure of a solution containing 0.0061 kg of benzoic acid in 0.05 kg of ether at the same temperature is 0.548×10^5 Pa. Calculate the molecular weight of benzoic acid in ether and the relative percentage error of the experiment relative to the value tabulated in handbooks.

5. A 7.5% aqueous solution of calcium chloride boils at the normal atmospheric pressure of 1.0133×10^5 Pa and 374 K. Calculate the factor i . The water vapour pressure at 374 K is 1.05×10^5 Pa.

6. Determine the percentage concentration of an aqueous solution of glycerol if the vapour pressure of this solution equals that of a solution containing 0.0089 kg NaNO_3 in 1 kg H_2O . The apparent degree of dissociation of NaNO_3 in the above solution is 64.9%.

7. The vapour pressure of a solution containing 2.21×10^{-3} kg CaCl_2 and 0.1 kg H_2O is 2319.8 Pa at 293 K, the water vapour pressure at the same temperature being 2338.5 Pa. Calculate the apparent molecular weight and the apparent degree of dissociation of CaCl_2 .

8. 0.1 kg of ether ($M = 74$) contains 0.01 kg of a non-volatile substance. The vapour pressure of this solution is 426 mm Hg at 293 K, while that of pure ether is 442 mm Hg at the same temperature. Calculate the molecular weight of the solute.

9. 0.0684 kg of sugar is dissolved in 1 kg of water ($M = 342$). Calculate the vapour pressure of this solution at 373 K. Determine its boiling point if the heat of evaporation of water at the boiling point is 2256.7×10^3 J/kg.

10. The boiling point of benzene is 353.36 K. Its molar heat of evaporation at the boiling point is 30 795 J/mole. Determine the ebullioscopic constant of benzene.

11. The boiling point of pure CS_2 is 319.2 K. A solution containing 0.217×10^{-3} kg of sulphur in 1.918×10^{-2} kg CS_2 boils at 319.304 K. The ebullioscopic constant of carbon disulphide is 2.37° . Determine the number of atoms in a sulphur molecule dissolved in carbon disulphide if the atomic weight of sulphur is 32.

12. 0.0106 kg of a solution contains 0.40×10^{-3} kg of salicylic acid dissolved in ethanol. The solution boils at a temperature 0.337° above the boiling point of pure ethanol. The molar increase in the boiling point of ethanol is 1.19° . Determine the molecular weight of salicylic acid.

13. Pure water boils at 373.2 K and atmospheric pressure. Determine the boiling point of a solution containing 3.291×10^{-3} kg of calcium chloride in 0.1 kg of water. The apparent degree of dissociation of CaCl_2 in the above solution is 68%. The ebullioscopic constant for water is 0.516° .

14. Determine the apparent degree of dissociation of HIO_3 in a solution containing 0.506×10^{-3} kg HIO_3 in 22.48×10^{-3} kg of ethanol. The solution boils at 351.624 K, whereas pure ethanol

boils at 351.46 K. The molar elevation in the boiling point of ethanol is 1.19° .

15. The freezing point of pure benzene is 278.500 K, and that of a solution containing 0.2242×10^{-3} kg of camphor in 3.055×10^{-2} kg of benzene is 278.254 K. The molar depression in the freezing point of benzene is 5.16° . Determine the molecular weight of camphor.

16. Glycerol is usually added to very weak aqueous solutions to avoid their freezing in winter. Assuming that Raoult's law is applicable to solutions of a similar concentration, calculate the amount of glycerol to be added so that a solution containing 0.1 kg of water does not freeze up to 268.16 K.

17. A solution containing 1.632×10^{-3} kg of trichloroacetic acid in 0.1 kg of benzene freezes at a temperature 0.350° below the freezing point of pure benzene. Determine whether trichloroacetic acid undergoes dissociation or association in the benzene solution and to what degree. The molar depression in the freezing point of benzene is 5.16° .

18. A solution containing 0.001 mole of zinc chloride in 1 kg of water freezes at 273.1545 K, while that containing 0.0819 mole of the same substance in 1 kg of water freezes at 272.7746 K. Calculate the factor i . The cryoscopic constant of water is 1.86° .

19. The melting point of phenol is 314 K. A solution containing 0.77×10^{-3} kg of acetanilide, $(C_8H_9O)N$, in 1.254×10^{-2} kg of phenol freezes at 310.25 K. Calculate the cryoscopic constant of phenol and its melting point (J/kg) in the solution if the molecular weight of acetanilide dissolved in benzene is consistent with its formula.

20. Determine the concentration of an aqueous glucose solution if the latter is isoosmotic, at 291 K, with a solution containing 0.5×10^3 mole/m³ $CaCl_2$, the apparent degree of dissociation of the latter at the above temperature being 65.4%.

21. 1×10^{-3} m³ of seawater contains primarily the following salts (kg): NaCl (27.2×10^{-3}), $CaSO_4$ (1.3×10^{-3}), $MgCl_2$ (3.4×10^{-3}), $CaCl_2$ (0.6×10^{-3}), and $MgSO_4$ (2.3×10^{-3}). Calculate the osmotic pressure of seawater at 298 K and compare the result with the value determined from the osmotic coefficient on the assumption that the above salts undergo complete dissociation.

22. The vapour pressure of a cane sugar solution in 1 kg of water is 98.88% that of pure water at the same temperature. Calculate the boiling point and osmotic pressure of this solution at 373 K, the solution density being 1×10^3 kg/m³.

23. Calculate the freezing point of a solution containing 7.308×10^{-3} kg of sodium chloride in 0.250 kg of water if the osmotic pressure of the solution is 2.1077×10^6 Pa at 291 K, its density is 1×10^3 kg/m³, and $l_{fus} = 333.48 \times 10^3$ J/kg.

24. The freezing point of a dilute aqueous solution of cane sugar is 272.171 K. The pure water vapour pressure at the same temperature is 568.6 Pa, and the heat of fusion of ice is 6029 J/mole. Calculate the vapour pressure of the solution.

25. Calculate the freezing point of an aqueous solution if its vapour pressure is 99% that of pure water at the same temperature. The heat of fusion of ice is 6029 J/mole.

26. Calculate the concentration of an aqueous solution of a substance in moles per kg of water if its vapour pressure at 373.58 K is 1.0109×10^5 Pa. The molar heat of evaporation of water is 40 193 J/mole; $P_{\text{H}_2\text{O}} = 1.0264 \times 10^5$ Pa at 373.58 K.

27. At 1.01×10^5 Pa, the boiling point of ether is 308 K. A solution containing 0.01094 kg of aniline in 0.1 kg of ether has a vapour pressure of 0.444×10^5 Pa at 288.46 K. The heat of evaporation of ether is 375.70×10^3 J/kg. Calculate the molecular weight of aniline in the solution.

28. Determine the percentage composition and molecular weight of a hydrocarbon proceeding from the following data: 0.2×10^{-3} kg of the substance yields 0.687×10^{-3} kg CO_2 and 0.1125×10^{-3} kg H_2O ; the freezing point of a solution containing 0.0925×10^{-3} kg of the substance in 0.01 kg of benzene is 0.354° below the freezing point of the latter. The cryoscopic constant of benzene is 5.16° .

29. An aqueous solution freezes at 271.5 K. Determine its boiling point and vapour pressure at 299 K. The cryoscopic constant of water is 1.86° , its ebullioscopic constant is 0.516° , and the water vapour pressure at 298 K is 3168 Pa.

30. The water vapour pressure at 293 K is 2338.5 Pa, and the vapour pressure of an aqueous solution is 2295.8 Pa. Determine its osmotic pressure at 313 K if the solution density at this temperature is 1010 kg/m³. The molecular weight of the solute is 60.

31. The freezing point of a solution containing 2.6152×10^{-3} kg of ethylene-glycol ether in 0.1 kg of water is 0.5535° below that of water. Determine the molecular weight of the ether if the heat of fusion of ice is 6029 J/mole.

32. Dry air is blown through 2.5×10^{-3} m³ of water at 283 K and 1.01×10^6 Pa. Determine the nitrogen and oxygen concentrations in the water when the state of equilibrium is reached, assuming that the solution is ideal. The Henry constants at 283 K are 677.14×10^7 Pa for nitrogen and 331.44×10^7 Pa for oxygen.

33. The solubility of gaseous hydrogen bromide in benzene at 303 K is characterized by the following values:

Molar fraction	0.000612	0.005459	0.01149	0.2335	0.02913	0.04713
P , Pa	1016.29	8460.64	25 771.00	39 053.77	46 832.41	75 537.79

Plot the solubility of HBr versus pressure and calculate the mean value of the constant in Henry's equation.

34. Determine the amount of hydrogen sulphide to be dissolved in 0.004 m^3 of water at 283 K and $50.66 \times 10^4 \text{ Pa}$. The water solubility of hydrogen sulphide at 283 K is 5.16 kg/m^3 at normal pressure.

35. The air composition by volume is as follows (%): O_2 , 20.96; N_2 , 78.1; Ar, 0.9; and CO_2 , 0.04. The solubilities of these gases in water at normal pressure are (m^3/m^3): O_2 , 0.0429; N_2 , 0.0209; Ar, 0.057; CO_2 , 1.424 ($10.132 \times 10^4 \text{ Pa}$, 278 K). Calculate the percentage ratio of the components of air dissolved in water at 278 K and $10.132 \times 10^4 \text{ Pa}$.

36. A vessel having a capacity of 0.01 m^3 contains oxygen at 292 K and 10^5 Pa . How much benzene is to be added to the vessel for the oxygen pressure to increase by $10.132 \times 10^4 \text{ Pa}$? The solubility of oxygen in benzene at 292 K and normal pressure is 0.233 kg/m^3 .

37. The Henry constants for oxygen in water at 273.2 and 283.2 K are 0.04889 and 0.03802 atm^{-1} , respectively. Calculate the enthalpy of the oxygen dissolved in water.

38. A 10 litre vessel with methane contains one litre of water at 298 K . The total pressure inside the vessel is $9.866 \times 10^4 \text{ Pa}$. How many grams of methane are dissolved in water?

39. The Henry constants for oxygen and nitrogen being dissolved in water at 273.2 K are 1.91×10^7 and $4.09 \times 10^7 \text{ mm Hg}$, respectively. Calculate the decrease in the freezing point of water, caused by the dissolution of air (80% N_2 and 20% O_2) at $1.0133 \times 10^5 \text{ Pa}$.

40. At 288 K , an aqueous solution of succinic acid, containing 12.1 g/litre of the latter, is at equilibrium with an ether solution containing 2.2 g/litre of the same acid. Determine the concentration of an ether solution of succinic acid, which is at equilibrium with an aqueous solution containing 4.84 g/litre of the acid. Succinic acid has a normal molecular weight both in water and in ether.

41. Distribution of acetic acid between carbon tetrachloride and water has resulted in the following concentrations (kg/m^3):

in CCl_4	2.92	3.63	7.25	10.7	14.1
in H_2O	48.7	54.2	76.4	93.0	107.0

Acetic acid has a normal molecular weight in the aqueous solution. Determine the molecular weight of acetic acid in the CCl_4 solution and its distribution coefficient.

42. Distribution of phenol between water and benzene has resulted in the following concentrations (mole/litre):

in H_2O	0.0316	0.123	0.327	0.750
in C_6H_6	0.077	0.159	0.253	0.390

Calculate the distribution coefficient K and exponent n in the equation for the distribution law.

43. Phenol has a normal molecular weight both in water and in amyl alcohol. At 298 K , a solution containing 10.53 g/litre of

phenol in amyl alcohol is at equilibrium with an aqueous solution containing 0.658 g/litre of phenol. Determine the weight percentage of phenol to be isolated from 0.5 litre of an aqueous solution, in which its concentration is 37.6 g/litre, by double extraction with amyl alcohol. For each extraction 0.1 litre of amyl alcohol is taken.

44. The coefficient of distribution of iodine between water and carbon tetrachloride at 298 K is 0.0117. Iodine has the same molecular weight in both solvents. How much carbon tetrachloride is to be taken in terms of volume so as to extract 99.9, 99.0, and 90.0% of iodine present in 0.5 litre of the aqueous solution in a single extraction?

45. How much iodine will remain in one litre of an aqueous solution which was saturated at 291 K after being shaken with 0.1 litre of carbon disulphide? The solubility of iodine in water at 291 K is 1 g per 3.616 litres. The coefficient of distribution of iodine between water and carbon disulphide is 0.001695. The molecular weight of iodine is the same in both solvents.

Multivariant Problems

1. At temperature T , the vapour pressure of a solution of an unknown non-volatile substance, whose concentration in the liquid solvent is c , equals P , Pa; the density of the solution being d . The

Variant	Weight percentage of the non-volatile substance	Molecular weight of the solvent	P , Pa	T , K	$d \times 10^{-3}$, kg/m ³
1	0.5	18	1 598	288.2	1.000
2	8	27	38 714	278	0.750
3	5	28	31 740	69	0.850
4	8.5	30	33 841	114	1.300
5	5	32	16 108	306.7	1.590
6	9	34	55 000	207	1.985
7	8	44	650 000	223	1.500
8	7	46	2 375	283.2	1.210
9	5	52	91 912	252.5	2.900
10	4.5	52.5	776	1991	6.800
11	5	58	35 896	303	3.560
12	6	64	7 328	216	1.590
13	3	68	12 420	149	1.780
14	3	78	5 807	283.2	0.750
15	6	81	49 431	194	1.210
16	5	83.5	84 990	119.6	2.160

Variant	Gas	Water solubility of the gas (g/100 g) at T, K										Coeff- cient in the SI system
		273	283	293	303	313	323	333	353	373		
1	Nitrogen	2.94	2.31	1.89	1.62	1.39	1.21	1.05	0.660	0	10 ³	
2	Nitrogen(II) oxide	9.83	7.56	6.17	5.17	4.39	3.76	3.24	1.98	0	10 ³	
3	Acetylene	0.200	0.150	0.117	0.094	—	—	—	—	—	—	
4	Hydrogen	1.92	1.74	1.60	1.47	1.39	1.29	1.18	0.79	0	10 ⁴	
5	Helium	—	1.75	1.74	1.72	1.70	1.69	—	—	—	10 ⁴	
6	Oxygen	6.95	5.37	4.34	3.59	3.09	2.66	2.27	1.38	0	10 ³	
7	Methane	3.95	2.96	2.32	1.90	1.59	1.36	1.14	0.695	0	10 ³	
8	Sulphur dioxide	22.8	16.2	11.3	7.80	5.41	—	—	—	—	—	
9	Hydrogen sulphide	0.707	0.511	0.385	0.298	0.236	0.188	0.148	0.077	0	—	
10	Carbon dioxide	0.335	0.232	0.169	0.125	0.097	0.076	0.058	—	—	—	
11	Carbon monoxide	4.40	3.48	2.84	2.41	2.08	1.80	1.52	0.980	0	10 ³	
12	Chlorine	1.46	0.997	0.729	0.572	0.459	0.393	0.329	0.223	0	—	
13	Hydrogen chloride	82.5	77.2	72.1	67.3	63.3	59.6	56.1	—	—	—	
14	Ethane	1.32	0.870	0.620	0.468	0.366	0.294	0.239	0.134	0	10 ²	
15	Ethylene	0.0284	0.0200	0.149	0.0118	—	—	—	—	—	—	

temperature dependence of the saturated vapour pressure over the liquid and the solid pure solvent is given in the table on pp. 178-182. (1) Calculate the molecular weight of the solute; (2) determine the molarity and molality of the solution; (3) calculate the osmotic pressure of the solution; (4) plot the $P = f(T)$ curve for the solution and solvent; (5) plot the temperature at which the vapour pressure over the pure solvent is P , Pa; (6) graphically determine the increase in the boiling point of the solution of concentration c at pressure P ; (7) calculate the ebullioscopic constant by all possible methods and compare the results at the normal boiling point ($T_{n.b.}$); (8) determine the depression in the freezing point of the solution; and (9) determine the cryoscopic constant.

2. Given the solubility of gases in water at different temperatures and a total pressure (of the gas and water vapour) of 1.01×10^5 Pa (see the table on 225), calculate the mean heat of solution of the gas in water and compare the result with the heat of condensation of the dissolved gas. Plot the water solubility of the gas as a function of temperature and pressure. Calculate the pressure range in which the solubility obeys Henry's law.

CHAPTER 14

Heterogeneous Equilibrium in Binary Systems Containing Liquid and Vapour Phases

Basic Equations and Symbols

In the case of ideal solutions, the concentrations of the i th component in the vapour and liquid phases are given by the equations

$$x_A^v = \frac{P_A^0}{P} x_A^{liq} \quad \text{and} \quad x_B^v = \frac{P_B^0}{P} x_B^{liq} \quad (14.1)$$

in which x_A^v and x_B^v stand for the molar fractions of components A and B, respectively, in the vapour phase, x_A^{liq} and x_B^{liq} are the molar fractions of components A and B in the liquid phase, P_A^0 and P_B^0 are the saturated vapour pressures over the pure components A and B, and P is the total vapour pressure over the solution.

The heat of evaporation of the mixture is given by the equation

$$\Delta H_{\text{evap}} = \Delta H_{\text{evap}, A} x_A^{liq} + \Delta H_{\text{evap}, B} x_B^{liq} \quad (14.2)$$

in which ΔH_{evap} is the heat of evaporation of one mole of the solution, $\Delta H_{\text{evap}, A}$ is the heat of evaporation of one mole of substance A, and $\Delta H_{\text{evap}, B}$ is the heat of evaporation of one mole of substance B.

As regards real solutions, the concentration of the i th component in the vapour phase is related to the activity of the same component

in the liquid phase as follows:

$$x_A^v = \frac{P_A^0}{P} a_A \quad \text{and} \quad x_B^v = \frac{P_B^0}{P} a_B \quad (14.3)$$

where a_A and a_B are the activities of the components in the solution.

The ratio between the weights of the vapour and liquid phases under a given set of conditions is determined, if the system is heterogeneous, according to the lever principle. If the weight percentage or fraction is plotted on the X axis of the liquidus boiling-point diagram, then

$$m^v/m = (w^{\text{liq}} - w)/(w^{\text{liq}} - w^v) \quad (14.4)$$

where m^v is the weight of the vapour phase, m is the weight of the system, w is the system's composition by weight, %, w^v is the composition of the vapour phase by weight, %, and w^{liq} is the composition of the liquid phase by weight, %. But if plotted on the X axis is the mole percentage or fraction, then

$$n^v/n = (x^{\text{liq}} - x)/(x^{\text{liq}} - x^v) \quad (14.5)$$

The saturated vapour pressure in the region of existence of a heterogeneous system whose components are finitely soluble in each other is

$$P = P_A + P_B \quad (14.6)$$

where P_A and P_B are partial pressures, and P is the total vapour pressure. In the heterogeneous region, $P_A = \text{const}$ and $P_B = \text{const}$. The saturated vapour pressure over a heterogeneous system whose components are mutually insoluble will be

$$P = P_A^0 + P_B^0, \quad (14.7)$$

where P_A^0 and P_B^0 stand for the saturated vapour pressure over the pure components A and B, respectively. The compositions of the vapour and condensate are identical:

$$n_A/n_B = x_A/x_B = P_A^0/P_B^0 \quad (14.8)$$

where n_A and n_B stand for the number of moles of components A and B, respectively. As can be inferred from Eq. (14.8), the molar ratio of components A and B in the vapour and condensate phases is independent of the ratio between these components in the initial mixture. The weight ratio of the components in the condensate is

$$m_A/m_B = M_A P_A^0 / (M_B P_B^0) \quad (14.9)$$

If one of the components during steam distillation is water, then

$$m_{\text{H}_2\text{O}} = m_B 18 P_{\text{H}_2\text{O}}^0 / (M_B P_B^0) \quad (14.10)$$

where $m_{\text{H}_2\text{O}}$ is the amount of steam necessary for distillation of m_{B} kg of component B. If in Eq. (14.10) $m_{\text{B}} = 1$ kg, then

$$m_{\text{H}_2\text{O}} = 18P_{\text{H}_2\text{O}}^0 / (M_{\text{B}}P_{\text{B}}^0) \quad (14.11)$$

where $m_{\text{H}_2\text{O}}$ is the amount of steam necessary for distillation of 1 kg of component B.

Exercises

1. At 313 K, the vapour pressures of dichloroethane and benzene are 2.066×10^4 and 2.433×10^4 Pa, respectively. What are the con-

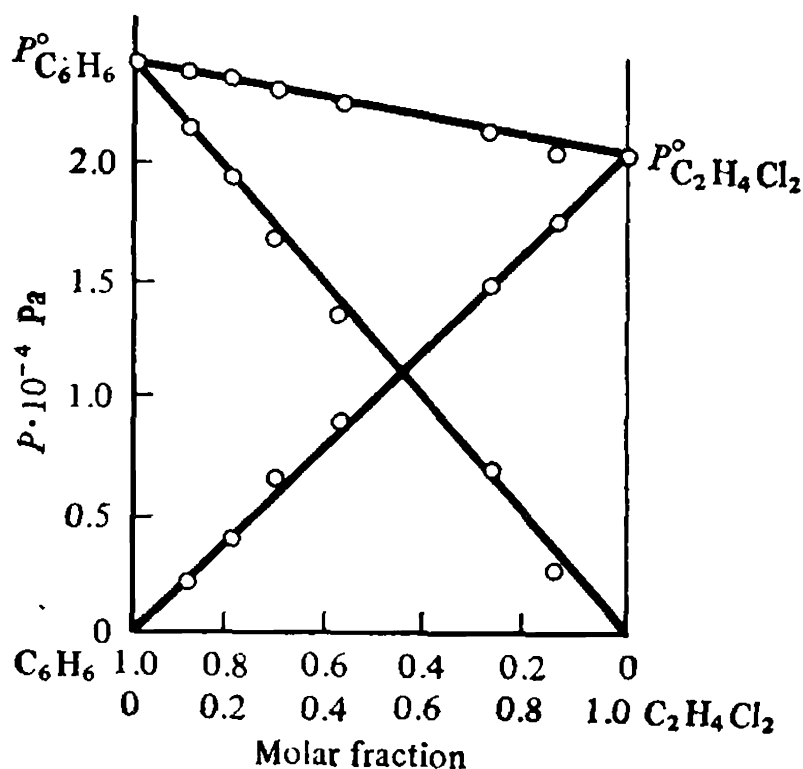


Fig. 20. Partial and total vapour pressures versus composition of a C_6H_6 - $\text{C}_2\text{H}_4\text{Cl}_2$ system at 313 K

clusions to be drawn from the following experimental partial pressures of dichloroethane and benzene at different concentrations:

$x_{\text{C}_6\text{H}_6}$	0.130	0.257	0.560	0.695	0.972	0.875
$P_{\text{C}_2\text{H}_4\text{Cl}_2} \times 10^{-4}, \text{ Pa}$	1.791	1.507	0.933	0.664	0.429	0.247
$P_{\text{C}_6\text{H}_6} \times 10^{-4}, \text{ Pa}$	0.292	0.648	1.347	1.663	1.933	2.140

Determine the composition of a mixture that will boil at 2.267×10^4 Pa. At what pressure will a mixture in which the mole percentage of benzene is 40 boil?

Solution. Plot pressure as a function of composition of the system at the constant temperature of 313 K (Fig. 20). On the X axis we shall have the molar fraction of dichloroethane, while plotted on the Y axis will be the vapour pressures of pure dichloroethane ($P_{\text{C}_2\text{H}_4\text{Cl}_2}^0$) and pure benzene ($P_{\text{C}_6\text{H}_6}^0$). Draw a straight line from the point corresponding to $P_{\text{C}_6\text{H}_6}^0$ to that corresponding to $P_{\text{C}_2\text{H}_4\text{Cl}_2}^0$, then do the same to connect the origin of coordinates to these two points.

This gives us the relationship between partial pressures and the composition of the mixture. To be more specific, the straight lines show the dependence of the total and partial saturated vapour pressures over the binary system on its composition, provided the solution obeys Raoult's law. The next step is to plot the points corresponding to the experimental values of partial pressures of the components and to the sum of these pressures. It can be seen from the plot that the solution may be considered as one obeying Raoult's law or as an ideal solution, within the experimental error. The plot indicates that a solution in which the mole percentage of dichloroethane is 62 will boil at 2.267×10^4 Pa, whereas a solution in which the mole percentage of benzene is 40 will boil at 2.200×10^4 Pa.

2. The following partial pressures over a dichloroethane-ethanol system have been obtained at 323 K:

$x_{C_2H_5OH}$	$P_{C_2H_5OH} \times 10^{-4}, \text{ Pa}$	$P_{C_2H_4Cl_2} \times 10^{-4}, \text{ Pa}$	$x_{C_2H_5OH}$	$P_{C_2H_5OH} \times 10^{-4}, \text{ Pa}$	$P_{C_2H_4Cl_2} \times 10^{-4}, \text{ Pa}$
0.1	1.139	2.860	0.6	2.155	2.464
0.2	1.773	2.740	0.7	2.260	2.249
0.3	1.953	2.686	0.8	2.417	1.843
0.4	2.025	2.652	0.9	2.672	1.147
0.5	2.085	2.585			

The saturated vapour pressure at this temperature is 2.960×10^4 Pa over pure ethanol and 3.113×10^4 Pa over pure dichloroethane. Calculate the total pressure over the system at all given concentrations. Plot the partial and total saturated vapour pressures as a function of composition of the system. Draw the appropriate conclusions as regards the nature of the solutions, the activity coefficients of their components, the change in volume during mixing, and the heat of mixing.

Solution. Proceeding from the partial pressures, calculate the total pressure over the system:

$x_{C_2H_5OH}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$P \times 10^{-4}, \text{ Pa}$	4.209	4.513	4.639	4.677	4.670	4.619	4.509	4.260	3.819

Having the values of partial and total saturated vapour pressures at all given concentrations, plot $P = f(x_{C_2H_5OH})$ (Fig. 21). It can be seen that the relations between the partial pressures of C_2H_5OH and $C_2H_4Cl_2$, on the one hand, and the total pressure, on the other, are nonlinear. The experimental pressures for all compositions are higher than that calculated according to Raoult's law. Consequently, the conclusion is that the C_2H_5OH - $C_2H_4Cl_2$ solution is not ideal and departs

from Raoult's law in the positive direction. The activity coefficients of the solution components exceed unity at all concentrations. Hence, when such a solution forms, its volume is greater than the sum of volumes of its components; the heat effect ΔH_{mix} is positive as heat is absorbed by the system during formation of the solution.

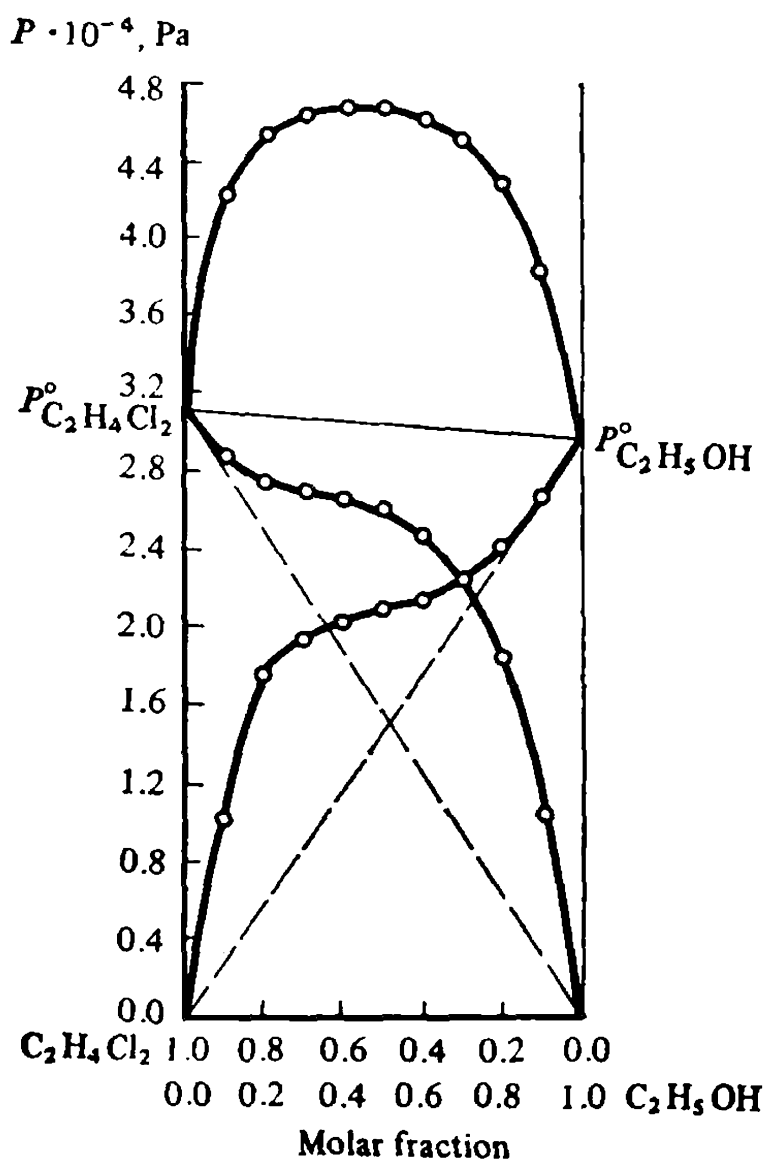


Fig. 21. Partial and total vapour pressures versus composition of a $\text{C}_2\text{H}_4\text{Cl}_2$ - $\text{C}_2\text{H}_5\text{OH}$ system at 313 K

3. The following values of partial saturated vapour pressure were derived in studying the equilibrium of a chloroform-diethyl ether system at 298 K:

$x_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5}$	0	0.2	0.4	0.6	0.8	1.0
$P_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5} \times 10^{-4}, \text{ Pa}$	0.000	0.460	1.287	2.666	4.093	5.333
$P_{\text{CHCl}_3} \times 10^{-4}, \text{ Pa}$	1.933	1.480	0.920	0.460	0.165	0.000

Plot partial and total saturated vapour pressures versus composition of the solution. Draw the appropriate conclusions as regards the departure from Raoult's law, the activity coefficients of the solution components at all concentrations, the change in volume during formation of the solution, and the heat of mixing.

Solution. Proceeding from the above partial pressures, calculate the total pressure and plot $P_{\text{CHCl}_3} = f(x)$, $P_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5} = f(x)$, and $P = f(x)$, where x is the molar fraction of ether (Fig. 22). As indicated by the curves, the solutions do not obey Raoult's law, no matter what their concentration is. The departure from Raoult's law is in the negative direction. The negative deviation from linearity diminishes and tends to zero as the concentration of the solution

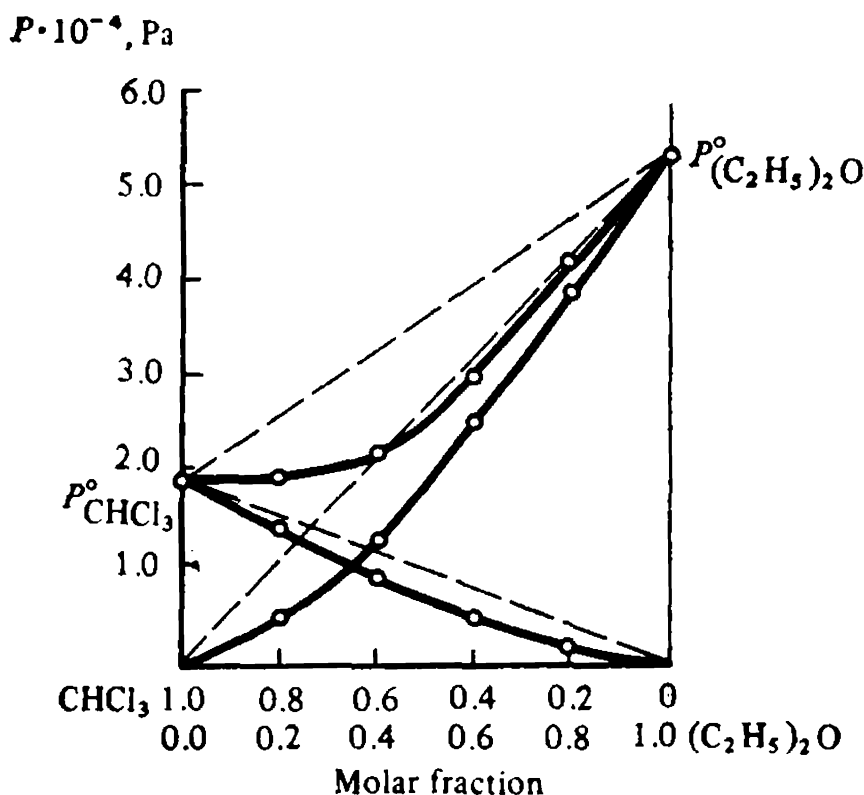


Fig. 22. Partial and total vapour pressures versus composition of a CHCl_3 - $(\text{C}_2\text{H}_5)_2\text{O}$ system at 298 K

component approaches unity. The activity coefficients of the solution component is less than unity at all concentrations. Hence, when solutions form, their volumes are smaller than the sum of volumes of their components; heat is released during formation of the solutions ($\Delta H_{\text{mix}} < 0$).

4. Plot the composition of the vapour phase versus that of the liquid phase for a dichloroethane-benzene system at 313 K if the following experimental values are known:

$x_{\text{C}_6\text{H}_6}$	0.130	0.257	0.560	0.695	0.792	0.875
$P_{\text{C}_2\text{H}_4\text{Cl}_2} \times 10^{-4}, \text{Pa}$	1.791	1.507	0.933	0.664	0.429	0.247
$P_{\text{C}_6\text{H}_6} \times 10^{-4}, \text{Pa}$	0.292	0.648	1.347	1.663	1.933	2.140

At 313 K, the vapour pressure of dichloroethane and benzene are 2.066×10^4 and 2.433×10^4 Pa, respectively.

Solution. Use Eq. (14.1) to calculate the composition of the vapour phase, proceeding from a certain composition of the liquid phase.

Calculate the total pressure over the system as the sum of partial pressures according to Dalton's equation:

$x_{\text{C}_6\text{H}_6}^{\text{liq}}$	0.130	0.257	0.560	0.695	0.792	0.875
$x_{\text{C}_6\text{H}_6}^{\text{v}}$	0.140	0.301	0.590	0.715	0.819	0.896
$P \times 10^{-4}, \text{ Pa}$	2.083	2.155	2.280	2.327	2.362	2.387

Proceeding from these results, plot the composition of the vapour phase versus that of the liquid phase: $x_{\text{C}_6\text{H}_6}^{\text{v}} = f(x_{\text{C}_6\text{H}_6}^{\text{liq}})$ (Fig. 23). The plot suggests that the concentration of benzene is greater in the vapour phase than in the liquid one. The difference between the

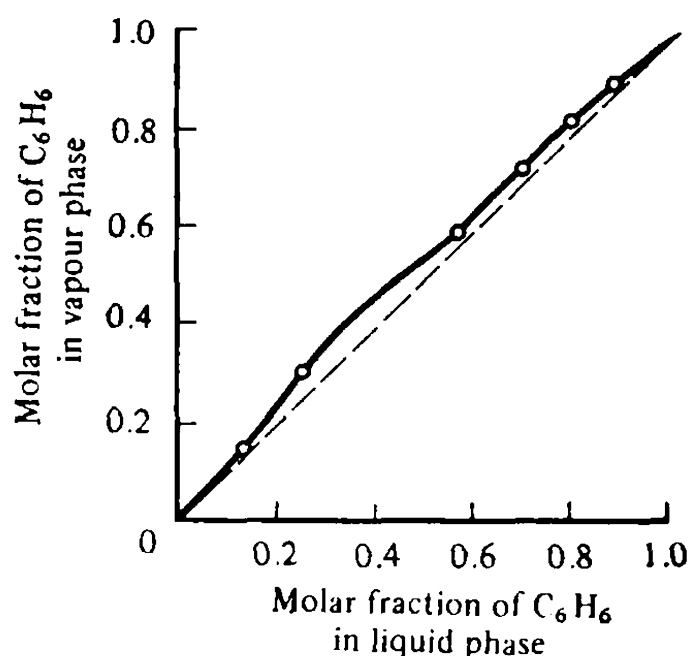


Fig. 23. Vapour phase composition versus that of the liquid phase for a C_6H_6 - $\text{C}_2\text{H}_4\text{Cl}_2$ system at 313 K

compositions of the two phases provides the basis for separation of two-component solutions.

5. Analyse the phase state of a CCl_4 - $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ system, using the boiling-point diagram (Fig. 24). Analyse the process of heating of a system in which the mole percentage of CCl_4 is 50.

Solution. Above the *abc* curve of composition of the saturated vapour all systems are in the vapour state. The systems are homogeneous and one-phase. Below the *adc* curve of composition of the boiling liquid all systems are in the liquid state. The systems are

also homogeneous and one-phase. The systems between the *abc* and *adc* curves are heterogeneous and consist of two phases, i.e. liquid and vapour. To determine the compositions of the equilibrium phases, draw an isotherm through the point corresponding to a given state since the phases at equilibrium must have the same temperatures. Intersection of the isotherm with the *adc* curve of composition of the boiling liquid gives the composition of the liquid phase, which is determined using the X axis. Intersection of the isotherm with the *abc* curve of the saturated vapour gives the composition of the vapour phase. For example, the system in which the mole percentage of CCl_4 is 40 at 338 K is heterogeneous (point *e*). It contains two phases which are at equilibrium. One of the phases is a boiling liquid containing 50% CCl_4 , and the other is a saturated vapour containing 24% CCl_4 . If the liquid system with 50% CCl_4 (point *f*) is heated to 338 K, it will start boiling. The molar composition of the vapour

at equilibrium with the boiling liquid will be 24% CCl_4 . The vapour contains less carbon tetrachloride than the liquid does. It is diethyl ether that passes primarily from the liquid phase into the vapour. Consequently, the liquid phase becomes depleted of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and its composition changes, as indicated by the arrows in Fig. 24. At the same time, the composition of the vapour at equilibrium with the liquid phase also changes. The latter change is indicated

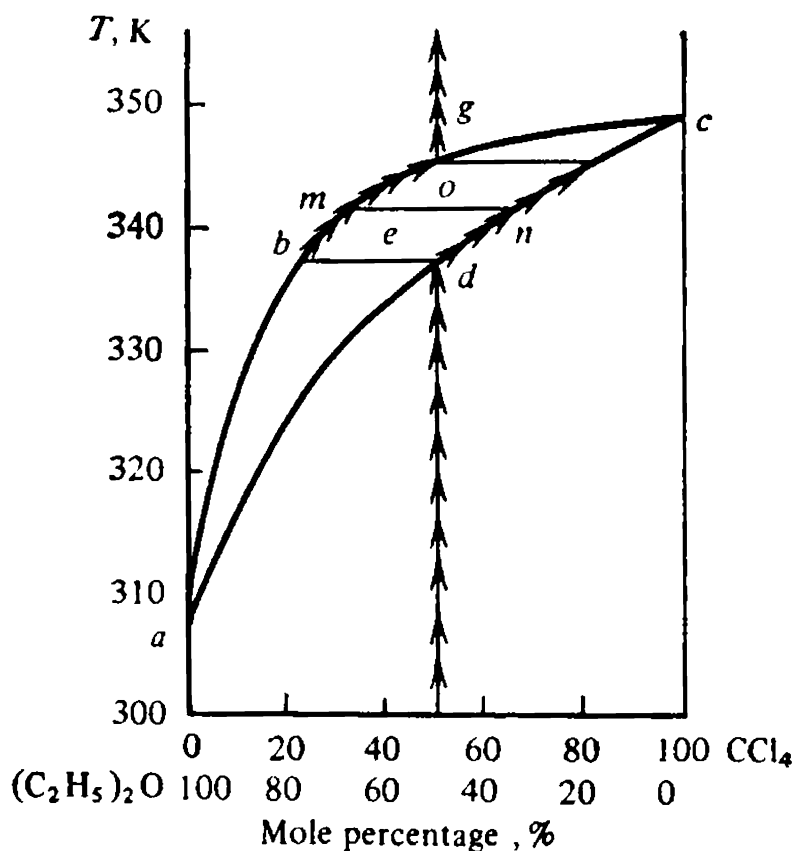


Fig. 24. Boiling-point diagram for a $(\text{C}_2\text{H}_5)_2\text{O}-\text{CCl}_4$ system at 1.0133×10^5 Pa

by arrows on the abc curve. At 342 K, the vapour and liquid phases will be at equilibrium. The molar compositions are 61% CCl_4 for the liquid phase and 35% CCl_4 for the vapour. The composition of the liquid and vapour phases as well as the phase equilibrium temperature will keep changing until the vapour composition becomes equal to that of the initial liquid (point f). At 354.4 K, the molar composition of the vapour will be 50% CCl_4 , and all of the liquid phase will evaporate. The system will become homogeneous. The molar composition of the last drop of the liquid will be 76% CCl_4 . Subsequent heating will not affect the composition of the vapour phase.

The cooling of the system with 50% CCl_4 will follow a reverse pattern. Let the molar composition of the initial system be 50% CCl_4 . At 350 K, this system (point g) is in the vapour state. As it cools down to 345.4 K, the system becomes heterogeneous and the first drop of liquid appears. Its molar composition is 81% CCl_4 . Since it is CCl_4 that passes predominantly from the vapour into the liquid phase, the vapour becomes depleted of CCl_4 and its composition will

change as indicated by the *abc* curve. The composition of the liquid phase at equilibrium with the vapour changes, too. This change follows the *adc* curve. As a result of changes in the liquid and vapour phase compositions, the liquefaction temperature is also altered. At 338 K, the composition of the liquid phase becomes equal to that of the initial vapour. At this temperature, the system becomes homogeneous and the last portion of vapour disappears. Further chilling will not affect the composition of the liquid phase.

6. Determine the quantities of CCl_4 and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ in the liquid and vapour phases (Fig. 24) if 1 kg of a system in which the mole percentage of CCl_4 is 50 is heated to 342 K.

Solution. Calculate the quantities of the substances in the liquid and vapour phases, using the lever principle. Since the molar composition is given as percentage in Fig. 24, use Eq. (14.5). First, determine the number of moles of the substance present in 1 kg of the system. To this end, calculate the mean molecular weight:

$$M_{\text{mean}} = 154 \times 0.5 + 74 \times 0.5 = 114$$

1 kg of the system contains

$$1000/114 = 8.772 \text{ moles } \text{CCl}_4 \text{ and } \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$$

The molar compositions of the coexisting phases at 342 K are (%): liquid CCl_4 (61), liquid $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (39), vaporous CCl_4 (35), vaporous $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (65). According to Eq. (14.5),

$$n^v = 8.772 (0.61 - 0.50)/(0.61 - 0.35) = 3.711 \text{ moles}$$

$$n^{\text{liq}} = 8.772 - 3.711 = 5.061 \text{ moles}$$

Knowing the composition of the phases, determine the number of moles of the components and their weight in each phase:

Phase	n	n_{CCl_4}	$w_{\text{CCl}_4}, \text{ kg}$	$n_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5}$	$w_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5}, \text{ kg}$
Liquid	5.061	3.087	0.475	1.974	0.146
Vapour	3.711	1.299	0.200	2.412	0.179

The sum will be: $0.475 + 0.200 + 0.146 + 0.179 = 1.000 \text{ kg}$.

7. Analyse the phase state of a CS_2 - CH_3COCH_3 system, using the boiling-point diagram (Fig. 25). Analyse the process of heating of a system in which the mole percentage of CH_3COCH_3 is 80.

Solution. The CS_2 - CH_3COCH_3 is characterized by departure from Raoult's law in the positive direction. In the case of a positive departure from this law, the activity coefficients of the solution components exceed unity, the volume increases during formation of the solution, and heat is absorbed: $\Delta V_{\text{mix}} > 0$, $\Delta H_{\text{mix}} > 0$.

Above the *abcde* curve of composition of the saturated vapour the system is homogeneous, the only phase being vapour. Below the *agcfe* curve of composition of the boiling liquid the system is also homogeneous, the only phase being liquid. Between the two curves the system is heterogeneous, the liquid and vapour phases being at equilibrium. The vapour composition is determined from the *abcde*

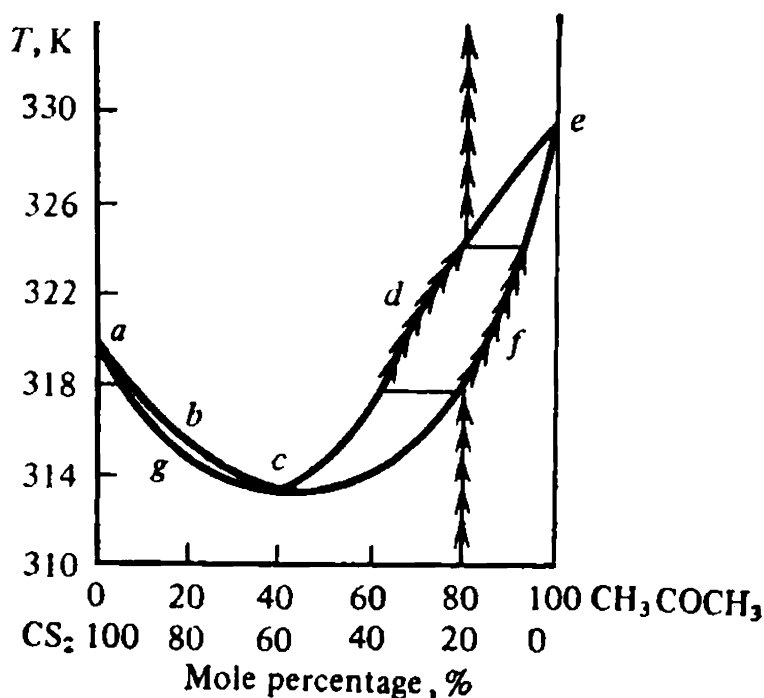


Fig. 25. Boiling-point diagram for a CS_2 - CH_3COCH_3 system at $1.0133 \times 10^5 \text{ Pa}$

curve, and that of the liquid is determined from the *agcfe* curve. Point *c* corresponds to the azeotropic mixture and is characterized by identical compositions of the liquid and vapour phases.

What happens when a system in which the mole percentage of CH_3COCH_3 is 80 is heated? Up to 317.5 K, the system is homogeneously liquid. At 317.5 K, the system starts boiling. The molar composition of the vapour is 62% CH_3COCH_3 . Since the vapour contains more carbon disulphide than the liquid does, the latter becomes depleted of carbon disulphide and its composition changes. At the same time, the boiling point of the liquid changes, too. The change in the composition of the liquid phase brings about a change in that of the saturated vapour at equilibrium with the liquid. The changes in phase compositions and temperature are indicated by arrows in the diagram. At 323.7, the vapour phase becomes equal in composition to the initial liquid system. At this temperature, the last drop of the liquid phase disappears. Its molar composition is 94% CH_3COCH_3 . The system then becomes homogeneous, and the vapour becomes heated without any change in the composition of the system.

As the system cools down, the boiling-point diagram shows reverse changes in the phase state of the system. At 323.7 K, liquefaction of the system begins. The molar composition of the first drop of liquid is 94% CH_3COCH_3 . It is acetone that passes predominantly from the vapour into the liquid phase. This means that carbon disulphide

becomes predominant in the vapour phase. The vapour composition and the condensation temperature change. At the same time, the composition of the liquid phase at equilibrium with the vapour changes, too. At 317.5 K, the liquid phase becomes equal in composition to the initial vapour phase. The liquefaction process is over, and the system becomes homogeneous.

8. Determine the component and its amount to be added to a CS_2 - CH_3COCH_3 system with 80% (mol.) CH_3COCH_3 so as to obtain an azeotropic mixture with 37% (mol.) CH_3COCH_3 . The weight of the system is 1 kg.

Solution. The initial mixture contains less carbon disulphide than the azeotropic one. Consequently, in order to obtain an azeotropic mixture from the initial system carbon disulphide must be added to it. First, calculate the number of moles in 1 kg of the initial system. To do this, determine the mean molecular weight of the initial solution:

$$M_{\text{mean}} = 76 \times 0.2 + 58 \times 0.8 = 61.6$$

1 kg of the solution contains a total of $1000/61.6 = 16.234$ moles or $16.234 \times 0.8 = 9.787$ moles CH_3COCH_3 and $16.234 \times 0.2 = 3.247$ moles CS_2 . Since it is carbon disulphide that has to be added, the number of moles of acetone in the system will remain invariable, and 9.787 moles of acetone in the azeotropic solution will constitute 37%. The remaining 63% will be carbon disulphide:

$$\begin{array}{ll} 9.787 \text{ moles} - 37\% & \\ x \text{ moles} - 63\% & x = 9.787 \times 63/37 = 16.664 \text{ moles of carbon} \\ & \text{disulphide} \end{array}$$

The solution contains 3.247 moles of carbon disulphide. Consequently, the amount to be added is $16.664 - 3.247 = 13.417$ moles or 1.020 kg CS_2 .

9. Determine the component and its amount to be isolated from 1 kg of a system in which the mole percentage of CH_3COCH_3 is 80 (Fig. 25) by rectification in the pure form.

Solution. To determine the number of moles of acetone and carbon disulphide in 1 kg of the system use the diagram in Fig. 25:

$$n_{\text{CS}_2} = 3.247 \text{ moles}, \quad n_{\text{CH}_3\text{COCH}_3} = 9.787 \text{ moles}$$

Since the stated composition is to the right of the azeotropic point, only acetone can be isolated by rectification in the pure form. All of carbon disulphide (3.247 moles) will pass into the azeotropic mixture in an amount of 63% (mol.). Acetone will account for the remaining 37% in the azeotropic solution:

$$\begin{array}{ll} 3.247 \text{ moles} - 63\% & \\ x \text{ moles} - 37\% & x = 3.247 \times 37/63 = 1.907 \text{ moles} \end{array}$$

Consequently, the azeotropic mixture will receive 1.907 moles of acetone, whereas isolated in the pure form can be $9.787 - 1.907 = 7.880$ moles or $7.880 \times 58 \times 10^{-3} = 0.457$ kg of acetone.

10. Determine the activities and activity coefficients of carbon disulphide and acetone in a $\text{CS}_2\text{-CH}_3\text{COCH}_3$ solution whose molar composition is 80% CH_3COCH_3 (Fig. 25) at 317.5 K.

Solution. The activities of the components can be determined with the aid of Eq. (14.3). The total pressure is constant and equal to 1.0133×10^5 Pa. To determine the saturated vapour pressure over the pure substances use Eq. (12.8):

$$\log \frac{P_2^0}{P_1^0} = \frac{\Delta H_{\text{evap}}}{2.3026R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Given the saturated vapour pressures at two temperatures, calculate the heat of evaporation:

$$\frac{\Delta H_{\text{evap}}}{2.3026R} = \frac{T_2 T_1}{T_2 - T_1} \log \frac{P_2^0}{P_1^0}$$

Find the saturated vapour pressure in the handbook. Determine the saturated vapour pressure over the pure substance at a third temperature:

$$\begin{aligned} \log P_3^0 = \log P_1^0 + \frac{\Delta H_{\text{evap}}}{2.3026R} \left(\frac{1}{T_1} - \frac{1}{T_3} \right) = \log P_1^0 \\ + \frac{T_1(T_3 - T_1)}{T_3(T_2 - T_1)} \log \frac{P_2^0}{P_1^0} \end{aligned}$$

Tabulate the results:

Substance	$P_1^0 \times 10^{-5}$, Pa	T_1 , K	$P_2^0 \times 10^{-5}$, Pa	T_2 , K	T_3 , K	$P_3^0 \times 10^{-5}$, Pa
CH_3COCH_3	0.5333	312.7	1.0133	329.7	317.5	0.6376
CS_2	0.5333	301.2	1.0133	319.7	317.5	0.9121

To determine the composition of the vapour phase use the boiling-point diagram (Fig. 25):

$$x_{\text{CS}_2} = 0.38, \quad x_{\text{CH}_3\text{COCH}_3} = 0.62$$

$$a_{\text{CS}_2} = 0.38 \times 1.0133 \times 10^5 / (0.9121 \times 10^5) = 0.422$$

$$\gamma_{\text{CS}_2} = 0.422 / 0.200 = 2.11$$

$$a_{\text{CH}_3\text{COCH}_3} = 0.62 \times 1.0133 \times 10^5 / (0.6376 \times 10^5) = 0.985$$

$$\gamma_{\text{CH}_3\text{COCH}_3} = 0.985 / 0.800 = 1.231$$

11. Butanol is finitely soluble in water. Analyse the phase state of a $\text{C}_4\text{H}_9\text{OH}-\text{H}_2\text{O}$ system, using the phase diagram (Fig. 26), at a constant pressure exceeding those of the saturated vapour over the pure components and the system as a whole. Follow the change in the phase state during cooling of a system in which the weight percentage of $\text{C}_4\text{H}_9\text{OH}$ is 68.

Solution. Since the external pressure exceeds the saturated vapour pressure over the system, it will not boil.

Consider first the phase state of the systems. Above the aKb curve all systems are homogeneous, the one phase being a liquid solution consisting of water and butanol. The systems under the aKb curve are heterogeneous and comprise two liquid phases. The aK curve

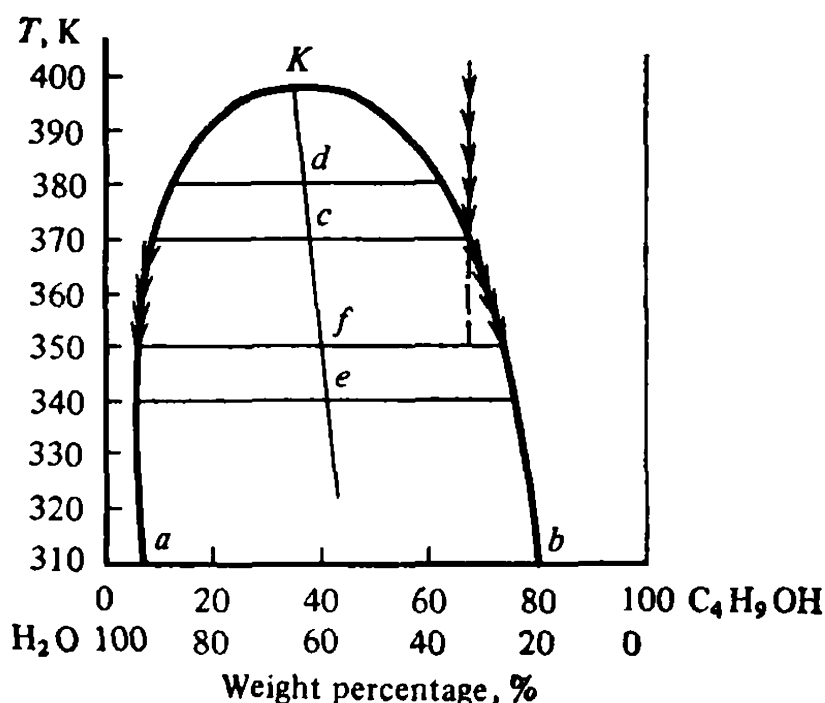


Fig. 26. Phase diagram for an $\text{H}_2\text{O}-\text{C}_4\text{H}_9\text{OH}$ system with limited solubility of components

corresponds to the compositions of butanol solutions in water, and the bK curve corresponds to those of water solutions in butanol. To determine the compositions of the liquid solutions coexisting in the state of equilibrium, draw an isotherm through the point corresponding to a particular composition at a given temperature. Intersection of the isotherm with the aK and bK curves gives the compositions of the solutions.

When a system containing 68% (wt) $\text{C}_4\text{H}_9\text{OH}$ is cooled down to 370 K, it becomes homogeneous. A second liquid phase appears at 370 K, and the system separates into two solutions. The composition of the new phase is 10% (wt) $\text{C}_4\text{H}_9\text{OH}$. As the system is cooled, it becomes less soluble. The compositions of the phases at equilibrium change as indicated by the arrows in the diagram. At 350 K, the weight percentage of $\text{C}_4\text{H}_9\text{OH}$ in the phases is 6 and 74, respectively.

12. Check whether Alekseev's straight diameter law applies to the butanol-water system of Fig. 26.

Solution. If the lines connecting the points at which the isotherms of 350 and 370 K are intersected by the aK and bK curves are divided in two and a straight line is drawn through the centres c and f , this line will pass through similar centres e , d , and so on and cross the phase equilibrium curve at the critical point K .

13. Determine the amounts of H_2O and C_4H_9OH in solutions of butanol in water and water in butanol if 1 kg of the system containing 68% (wt) C_4H_9OH is cooled down to 350 K.

Solution. The amounts of the coexisting phases are to be determined according to the lever principle. Since plotted on the X axis is weight percentage, the lever principle is given by Eq. (14.4). To determine the compositions of the coexisting phases at 350 K use the diagram of Fig. 26.

Phase	Curves	Weight percentage	
		H_2O	C_4H_9OH
1st	aK	94	6
2nd	bK	26	74

$$m_1/m = (74 - 68)/(74 - 6)$$

where m_1 is the weight of the 1st phase and m is the total weight of the system; $m = 1$ kg; $m_1 = 0.088$ kg; $m_2 = 1 - 0.088 = 0.912$ kg. Hence, the weights of water and butanol in the 1st and 2nd phases will be:

Phase	Weight, kg	
	C_4H_9OH	H_2O
1st	$0.088 \times 0.06 = 0.0053$	$0.088 \times 0.94 = 0.0827$
2nd	$0.912 \times 0.74 = 0.6749$	$0.912 \times 0.26 = 0.2371$

The total weight of the system is $0.0053 + 0.0827 + 0.6749 + 0.2371 = 1.000$ kg.

14. Plot approximately the saturated vapour pressure versus the composition of the $C_4H_9OH-H_2O$ system at 350 K, proceeding from the phase diagram of Fig. 26. Calculate the activity and activity coefficient of H_2O in the coexisting phases at 350 K.

Solution. According to the Clapeyron-Clausius equation (12.8) and the values given in the handbook, the saturated vapour pressure over pure butanol at 350 K will be as follows:

$T, \text{ K}$	343.3	357.5
$P_{\text{C}_4\text{H}_9\text{OH}}^0 \times 10^{-5}, \text{ Pa}$	0.1333	0.2666

$$\log P_3^0 = \log P_1^0 + \frac{T_1(T_3 - T_1)}{T_3(T_2 - T_1)} \log \frac{P_2^0}{P_1^0} = 4.1248$$

$$+ \frac{343.3(350 - 343.3)}{350(357.5 - 343.3)} \log \frac{0.2666 \times 10^5}{0.1333 \times 10^5} = 4.2641 \quad P_3^0 = 1.8370 \times 10^4 \text{ Pa}$$

Find the saturated water vapour pressure in the handbook: at 350 K, $P^0 = 4.2064 \times 10^4 \text{ Pa}$.

Convert the weight percentages for the phases in the heterogeneous region at 350 K into molar fractions: for the water layer, 6% $\text{C}_4\text{H}_9\text{OH}$

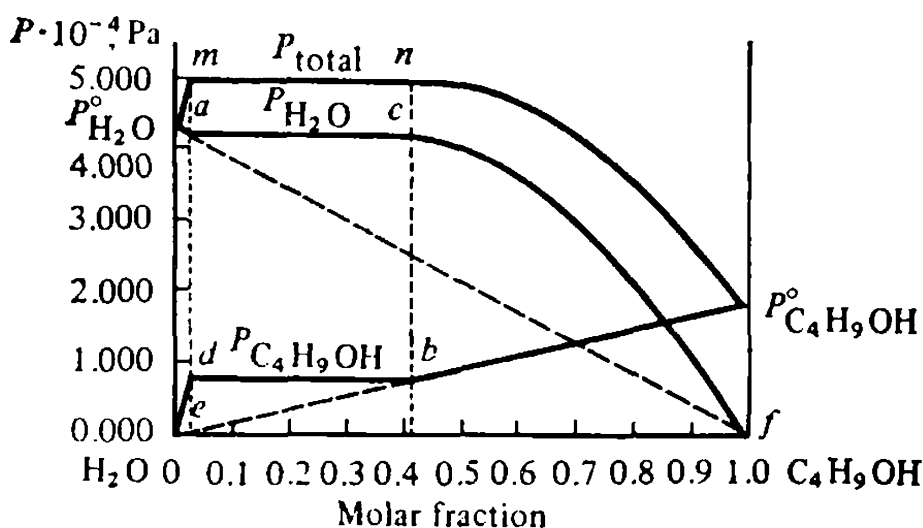


Fig. 27. Partial and total pressures versus composition of an $\text{H}_2\text{O}-\text{C}_4\text{H}_9\text{OH}$ system with limited solubility at 350 K

correspond to $x_{\text{C}_4\text{H}_9\text{OH}} = 0.0153$; for the alcohol layer, 74.0% $\text{C}_4\text{H}_9\text{OH}$ correspond to $x_{\text{C}_4\text{H}_9\text{OH}} = 0.4091$. Plot (Fig. 27) $P_{\text{C}_4\text{H}_9\text{OH}}^0 = 1.8370 \times 10^4 \text{ Pa}$ for $x_{\text{C}_4\text{H}_9\text{OH}} = 1$ on the Y axis. Connect this point to the origin of coordinates $x_{\text{C}_4\text{H}_9\text{OH}} = 0$ by a dashed line which represents the relationship between the partial pressure of butanol and composition, obeying Raoult's law.

Similarly, plot $P_{\text{H}_2\text{O}}^0 = 4.2064 \times 10^4 \text{ Pa}$ for $x_{\text{C}_4\text{H}_9\text{OH}} = 0$ on the Y axis. Draw a dashed line to connect this point with the origin of coordinates $x_{\text{C}_4\text{H}_9\text{OH}} = 1$. This line obeys Raoult's law and represents the relationship between the partial pressure of water and composition. Since according to the first condition of selecting the standard state $\gamma \rightarrow 1$ at $x \rightarrow 1$, it may be assumed approximately that in the homogeneous regions the relations $P_i = f(x_i)$ coincide with those obeying Raoult's law. In Fig. 27, this corresponds to the portions $P_{\text{H}_2\text{O}}^0 a$ and $P_{\text{C}_4\text{H}_9\text{OH}}^0 b$. Since the partial pressures of the

components above the heterogeneous region are independent of concentration, draw horizontal straight lines ac and bd from points a and b . Then the partial pressure relations in the homogeneous region become complex but the curves representing them must be convex upward. Plot approximately these curves (de and cf).

The total pressure equals the sum of partial pressures. Draw the line representing the relationship between the total pressure over

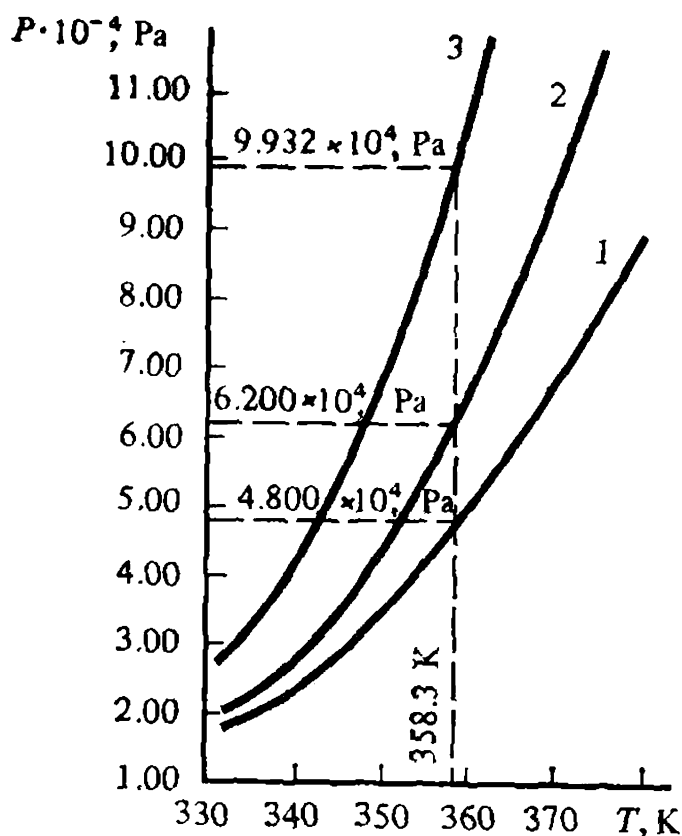


Fig. 28. Saturated vapour pressure versus temperature for $\text{C}_6\text{H}_5\text{CH}_3$ (1), H_2O (2), and $\text{H}_2\text{O}-\text{C}_6\text{H}_5\text{CH}_3$ system (3)

the system and its composition: $P_{\text{H}_2\text{O}}^0 m n P_{\text{C}_4\text{H}_9\text{OH}}^0$. The total pressure over the heterogeneous system will be constant and equal to 4.894×10^4 Pa. This means that the compositions from 0.0153 to 0.4091 $\text{C}_4\text{H}_9\text{OH}$ at 4.894×10^4 Pa will boil at 350 K.

With the H_2O concentration being $1 - 0.0153 = 0.9847$, the activity of water is numerically equal to the concentration, that is $a'_{\text{H}_2\text{O}} = 0.9847$, and the solution obeys Raoult's law. The activity coefficient of water is $\gamma' = 0.9847/0.9847 = 1$. Since the chemical potential of water in equilibrium phases is the same, then

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}^0 + RT \ln x'_{\text{H}_2\text{O}} + RT \ln \gamma'_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}^0 + RT \ln x''_{\text{H}_2\text{O}} + RT \ln \gamma''_{\text{H}_2\text{O}}$$

Consequently, the activity coefficient of water in a solution where the concentration of the latter is $(1 - 0.4091) = 0.5909$ will be $\gamma''_{\text{H}_2\text{O}} = 0.9847/0.5909 = 1.6664$. The activity coefficient exceeds unity, the departure from Raoult's law is positive: $\Delta V_{\text{mix}} > 0$; $\Delta H_{\text{mix}} > 0$.

15. To purify toluene it is subjected to steam distillation at an external pressure of 9.932×10^4 Pa. At what temperature will the system boil if toluene is virtually insoluble in water? Use the following data for the calculation:

$T, \text{ K}$	333	343	353	363	373
$P_{\text{H}_2\text{O}}^0 \times 10^{-4}, \text{ Pa}$	2.058	3.219	4.893	7.244	10.469
$P_{\text{C}_6\text{H}_5\text{CH}_3}^0 \times 10^{-4}, \text{ Pa}$	1.860	2.698	3.862	5.394	7.429

Solution. Plot the temperature dependence of the saturated vapour pressures of water (1) and toluene (2) (Fig. 28). Adding up the pressures $P_{\text{H}_2\text{O}}^0$ and $P_{\text{C}_6\text{H}_5\text{CH}_3}^0$ according to Eq. (14.6) gives the total saturated vapour pressure over the heterogeneous system (3). Use the plot to find the temperature at which the saturated vapour pressure over the heterogeneous system becomes equal to the external pressure of 9.932×10^4 Pa. The system will boil at 358.3 K.

16. Proceeding from the temperature dependence of the saturated vapour pressure (Fig. 28), calculate the amount of steam necessary for distillation of 1 kg of toluene at an external pressure of 9.932×10^4 Pa.

Solution. Use the plot to find the saturated vapour pressures of toluene and water at 358.3 K. They equal 4.800×10^4 Pa for toluene and 6.200×10^4 Pa for water. According to Eq. (14.11), to distill 1 kg of toluene will require the following amount of steam:

$$m_{\text{H}_2\text{O}} = 6.200 \times 10^4 \times 18 / (4.800 \times 10^4 \times 92) = 0.253 \text{ kg}$$

Problems

1. The solution of benzene in toluene may be considered ideal. At 300 K, the saturated vapour pressure is 1.603×10^4 Pa over benzene and 0.489×10^4 Pa over toluene. Plot the partial pressures of benzene and toluene as well as the total pressure over the benzene-toluene system versus the molar composition of the solution expressed in fractions. Determine the vapour pressure over a system containing 30% (mol.) benzene. What will be the partial pressure and total pressure over a solution containing 0.1 kg of each substance? Calculate the change in entropy and free energy during formation of one mole of a solution in which the mole percentage of benzene is 30 at 300 K.

2. The experimentally determined partial pressures over an acetone-chloroform system at 308.2 K, as a function of composition, are as follows:

x_{CHCl_3}	0.0	0.2	0.4	0.6	0.8	1.0
$P_{\text{CHCl}_3} \times 10^{-4}, \text{ Pa}$	0	0.453	1.093	1.973	3.000	3.906
$P_{\text{CH}_3\text{COCH}_3} \times 10^{-4}, \text{ Pa}$	4.586	3.600	2.440	1.360	0.560	0

Proceeding from these values, plot the partial and total pressures over the system versus its composition. Compare the found relations with those for solutions obeying Raoult's law. Determine the total pressure at which a system with 50% (mol.) chloroform will boil at 308.2 K. At what pressure would the system boil if the solution were ideal?

3. The experimentally determined partial pressures over an acetone-carbon disulphide system at 308.2 K, as a function of composition, are as follows:

x_{CS_2}	0	0.2	0.4	0.6	0.8	1.0
$P_{\text{CS}_2} \times 10^{-4}, \text{ Pa}$	0	3.733	5.040	5.666	6.133	6.826
$P_{\text{CH}_3\text{COCH}_3} \times 10^{-4}, \text{ Pa}$	4.586	3.866	3.400	3.066	2.533	0

Plot the partial and total pressures over the system versus its composition in molar fractions. Compare the resulting relation with that for ideal solutions, derived in accordance with Raoult's law. Determine the compositions of the system at which the total vapour pressure over it at 308.2 K will be $8.5 \times 10^4 \text{ Pa}$. What would be the pressure over the system if the solution were ideal?

4. Calculate the total vapour pressure over a system containing 0.078 kg of benzene and 0.076 kg of carbon disulphide, at each of the temperatures given below, if the solution is assumed to be ideal:

$T, \text{ K}$	293	313	353
$P_{\text{C}_6\text{H}_6}^0 \times 10^{-4}, \text{ Pa}$	1.020	2.466	10.066
$P_{\text{CS}_2}^0 \times 10^{-4}, \text{ Pa}$	3.960	8.226	27.064

The total pressures determined experimentally at these temperatures are 2.746×10^4 , 5.760×10^4 , and $19.665 \times 10^4 \text{ Pa}$, respectively. Calculate the deviations from the pressure over an ideal solution for each temperature. When is the behaviour of the solution closer to ideal—at a higher or at a lower temperature?

5. Plot the content of benzene in the vapour phase versus that in the liquid phase. Determine the benzene content in the vapour phase if its mole percentage in the liquid phase is 40. Benzene and toluene form solutions closely approaching ideal ones. At 293 K, the benzene and toluene pressures are 1.020×10^4 and $0.327 \times 10^4 \text{ Pa}$, respectively.

6. The vapour pressures of substances A and B at 323 K are 4.666×10^4 and $10.132 \times 10^4 \text{ Pa}$, respectively. Calculate the composition of the vapours at equilibrium with the solution assuming that the solution formed by mixing 0.5 mole A with 0.7 mole B is ideal.

7. Calculate, in molar fractions, the composition of a solution boiling at 373 K and $10.133 \times 10^4 \text{ Pa}$ if CCl_4 and SnCl_4 form ideal

solutions. The CCl_4 and SnCl_4 vapour pressures at 373 K are 19.332×10^4 and 6.666×10^4 Pa, respectively. Determine the composition of the first vapour bubble in molar fractions. What will be the composition of the last drop of the liquid if the solution evaporates completely?

8. Calculate the composition of the vapours over a solution containing 0.5 mole of benzene and an equal amount of toluene from the following temperature dependence of the saturated vapour pressure for benzene and toluene:

$T, \text{ K}$	330	350	380	420
$P_{\text{C}_6\text{H}_6}^0 \times 10^{-4}, \text{ Pa}$	5.2	9.3	21.3	55.5
$P_{\text{C}_6\text{H}_5\text{CH}_3}^0 \times 10^{-4}, \text{ Pa}$	1.6	3.8	9.3	25.8

Is Vrevsky's first law applicable here? Assume that the solution is ideal.

9.* Assuming that the solution of *n*-heptane and *n*-octane is ideal, draw its boiling-point diagram proceeding from the heats of evaporation and boiling points given in the handbook.

10. What quantities of vapour and liquid phase will be at equilibrium if 1 kg of a $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5\text{-CCl}_4$ solution with 30% (mol.) CCl_4 is heated to 333 K? The molar composition of the liquid phase is 37% CCl_4 and that of the vapour is 16% CCl_4 . The boiling-point diagram can be found in the handbook.

11. What component and in what amount is to be added to 1 kg of an $\text{HNO}_3\text{-H}_2\text{O}$ system containing 60% (mol.) HNO_3 in order to obtain an azeotropic mixture? The boiling-point diagram can be found in the handbook.

12. The partial pressure of CH_3OH over its aqueous solution with $x_{\text{CH}_3\text{OH}} = 0.25$ is 12.5×10^5 Pa at 313.1 K and 30.5×10^3 Pa at 332.6 K. Determine the partial molar heat of evaporation of CH_3OH from a solution with $x_{\text{CH}_3\text{OH}} = 0.25$.

13. Determine the partial molar heat of solution of CH_3OH in a $\text{CH}_3\text{OH-H}_2\text{O}$ solution with $x_{\text{CH}_3\text{OH}} = 0.25$ at 332.6 K if the molar heat of evaporation of CH_3OH from a $\text{CH}_3\text{OH-H}_2\text{O}$ solution with $x_{\text{CH}_3\text{OH}} = 0.25$ at 332.6 K is 39.6 kJ/mole. Find the heat of evaporation of pure methanol in the handbook.

14. Prove that in an azeotropic solution $\gamma_A = P/P_A^0$ and $\gamma_B = P/P_B^0$, where P is the total pressure over the system; γ_A , γ_B , P_A^0 , and P_B^0 corresponding to the boiling point of the azeotropic solution.

15. Determine the activity coefficients and activities of CCl_4 and $\text{C}_2\text{H}_5\text{OH}$ in a solution with $x_{\text{CCl}_4} = 0.63$ at 337 K. The total pressure is 10.133×10^4 Pa. Find the necessary data in the handbook. The boiling-point diagram of the $\text{CCl}_4\text{-C}_2\text{H}_5\text{OH}$ system find in the handbook.

16*. Formic acid and water form an azeotropic solution with $x_{\text{H}_2\text{O}} = 0.467$ at 380.8 K. The total pressure is 10.133×10^4 Pa.

Determine the activity coefficients and activities of formic acid and water in the azeotropic solution. The heat of evaporation of formic acid is $\Delta H_{\text{HCOOH}} = 22.24 \text{ kJ/mole}$ at $T_{\text{n.b.}} = 373.9 \text{ K}$. The heat of evaporation of water at $T_{\text{n.b.}}$ is $\Delta H_{\text{H}_2\text{O}} = 40.66 \text{ kJ/mole}$. Determine whether the departure of the system from Raoult's law is positive or negative.

17. During steam distillation of bromobenzene the boiling starts at $10.133 \times 10^4 \text{ Pa}$ and 368.3 K . Bromobenzene is almost insoluble in water, while the partial pressures of water and bromobenzene at the above temperature are 8.519×10^4 and $1.613 \times 10^4 \text{ Pa}$, respectively. Calculate the amount of bromobenzene passing into the distillate together with 1 kg of water.

18. The vapour pressure over a system consisting of two immiscible liquids, aniline and water, is $9.999 \times 10^4 \text{ Pa}$ at 371 K . The water vapour pressure at this temperature is $9.426 \times 10^4 \text{ Pa}$. How much water is to be taken for distillation of 1 kg of aniline at an external pressure of $9.999 \times 10^4 \text{ Pa}$?

19. The saturated vapour pressure over a system consisting of two immiscible liquids, diethylaniline and water, is $10.133 \times 10^4 \text{ Pa}$ at 372.4 K . How much steam is required for distillation of 0.1 kg of diethylaniline if the water vapour pressure at this temperature is $9.919 \times 10^4 \text{ Pa}$?

20. Determine the amount of steam necessary for distillation of 0.1 kg of naphthalene at normal pressure. At what temperature will the distillation take place? Use the relation $P = f(T)$ for the calculation:

$T, \text{ K}$	368	369	370	371	372	373
$P_{\text{H}_2\text{O}}^0 \times 10^{-4}, \text{ Pa}$	8.451	8.767	9.094	9.430	9.775	10.132
$P_{\text{C}_{10}\text{H}_8}^0 \times 10^{-4}, \text{ Pa}$	0.203	0.211	0.221	0.233	0.245	0.260

Naphthalene is virtually insoluble in water.

21. The temperature dependence of the saturated vapour pressure (Pa) of furfural is given by the equation

$$\log P = 10.084 - 2209/T$$

Determine the temperature at which steam distillation of furfural will take place at normal pressure. Determine the amount of steam necessary for distillation of 1 kg of furfural. Find the temperature dependence of the saturated water vapour pressure in the handbook. Furfural is barely soluble in water.

Multivariant Problems

1. The temperature dependence of the compositions of a liquid phase and the vapour at equilibrium with the latter at a constant pressure is known for a binary A-B system. The molar composition x

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x - liquid phase	y - vapour phase	
1	A = HNO ₃ B = H ₂ O	10.133	0.0	0.0	373
			8.4	0.6	379.5
			12.3	1.8	385
			22.1	6.6	391.5
			30.8	16.6	394.6
			38.3	38.3	394.9
			40.2	60.2	394
			46.5	75.9	391
			53.0	89.1	385
			61.5	92.1	372
			100.0	100.0	357
2	A = HNO ₃ B = CH ₃ COOH	10.79	0.0	0.0	391.1
			10.0	3.0	395.1
			20.0	8.0	399.5
			33.3	34.0	401.6
			40.0	47.0	400.3
			50.0	82.0	393.3
			60.0	96.0	378
			100.0	100.0	358.3
3	A = HF B = H ₂ O	10.133	4.95	0.8	374.6
			9.2	1.8	375.8
			18.9	6.4	379.8
			22.8	10.6	381.4
			27.9	17.8	383.3
			33.8	30.5	384.7
			34.4	32.1	385.0
			35.8	35.8	385.4
			39.7	47.5	384.4
			44.4	63.3	381.7
			50.3	81.0	374.7
			52.2	86.2	371.9
			56.0	92.2	365.9
			58.2	95.8	359.6
			61.7	98.9	352.0
			79.8	99.2	318.1
			87.9	99.5	306.5
			100.0	100.0	292.4

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x - liquid phase	y - vapour phase	
4	A = H ₂ O B = C ₆ H ₄ O ₂ (furfural)	10.133	0.0	0.0	435.0
			2.0	10.0	431.8
			4.0	19.0	427.8
			6.0	36.0	419.0
			8.0	68.0	395.5
			10.0	81.1	382.5
			20.0	89.0	373.6
			30.0	90.5	371.7
			50.0	90.8	370.9
			90.8	90.8	370.9
			96.0	90.8	370.9
			98.0	92.0	371.1
			99.0	94.5	371.6
			100.0	100.0	373.0
5	A = H ₂ O B = C ₄ H ₁₀ O (<i>n</i> -butanol)	10.133	3.9	26.7	384.5
			4.7	29.9	383.6
			5.5	32.3	382.6
			7.0	35.2	381.8
			25.7	62.9	370.9
			27.5	64.1	370.2
			29.2	65.5	369.7
			30.5	66.2	369.3
			49.6	73.6	366.5
			50.6	74.0	366.4
			55.2	75.0	365.9
			57.7	75.0	365.8
			97.5	75.2	365.7
			98.0	75.6	366.0
			98.8	80.8	366.7
			99.2	84.3	368.4
			99.4	88.4	369.8
6	A = H ₂ O B = C ₄ H ₁₀ O (<i>iso</i> -butanol)	10.133	13.5	40.1	370.8
			15.0	42.0	370.1
			15.9	43.7	369.6

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x-liquid phase	y-vapour phase	
6	A = H ₂ O B = C ₄ H ₁₀ O (<i>iso</i> -butanol)	10.133	17.2	44.6	369.0
			39.7	62.6	363.3
			40.5	63.3	363.2
			56.4	66.0	362.5
			60.5	66.7	362.4
			67.0	67.0	362.2
			97.5	67.2	362.5
			97.8	67.3	363.1
			98.6	71.4	364.5
			99.1	78.2	366.4
			99.8	95.7	371.9
7	A = H ₂ O B = C ₅ H ₁₂ O (2-methyl-3-butyl-2-ol)	10.246	0.0	0.0	377.5
			18.9	42.7	367.8
			34.2	55.3	365.3
			53.8	63.4	364.3
			66.7	65.7	364.1
			75.7	66.9	364.2
			82.4	67.5	364.25
			87.5	68.1	364.3
			91.6	69.1	364.4
			94.9	70.3	364.8
			97.7	75.7	366.4
			99.5	91.0	369.0
			100.0	100.0	373.3
8	A = CS ₂ B = CH ₃ COCH ₃	10.133	0.0	0.0	329.2
			1.9	8.3	327.0
			4.8	18.5	324.4
			13.4	35.1	319.6
			18.6	44.3	317.0
			29.1	52.8	314.4
			38.0	57.4	313.3
			44.8	59.8	312.8
			53.6	62.7	312.3
			65.3	66.1	312.1
			78.9	70.5	312.3
			87.9	76.0	313.5
			96.8	88.6	316.5
			100.0	100.0	319.3

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x -liquid phase	y -vapour phase	
9	A = CH ₃ OH B = CCl ₄	10.133	0.0	0.0	349.7
			0.2	2.0	349.1
			0.4	12.0	345.4
			1.3	24.2	340.6
			1.7	26.4	339.9
			3.0	38.3	335.0
			5.1	44.5	332.4
			10.7	49.0	330.2
			12.4	50.0	330.0
			24.8	52.2	329.3
			40.1	53.7	328.8
			45.3	54.1	328.8
			55.0	55.2	327.7
			56.6	55.2	328.7
			72.5	59.1	329.0
			76.4	60.3	329.4
			81.3	63.0	329.8
			83.8	64.9	330.1
			88.3	69.6	331.2
			91.8	75.3	332.5
			94.8	82.3	333.9
			97.9	91.0	335.8
			99.3	96.7	337.1
			100.0	100.0	337.7
10	A = CH ₃ OH B = C ₆ H ₆	9.670	0.0	0.0	351.6
			2.4	17.5	341.2
			3.6	30.1	336.9
			4.7	43.5	333.3
			5.9	51.1	330.7
			6.3	53.4	330.3
			9.2	54.6	329.8
			24.9	59.9	329.4
			64.5	64.5	329.4
			78.5	66.6	329.9
			84.7	71.3	330.6
			90.2	77.1	330.3
			94.1	84.4	332.6
			98.3	93.6	334.9
			100.0	100.0	336.1

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x – liquid phase	y – vapour phase	
11	A = CH ₃ OH B = C ₆ H ₆	10.133	0.0	0.0	363.2
			2.8	31.0	342.4
			5.0	39.5	339.8
			5.7	42.0	338.7
			9.0	48.5	334.4
			11.8	56.5	332.0
			27.0	57.5	331.0
			44.0	58.5	330.8
			58.6	61.0	330.7
			69.5	62.5	330.6
			81.7	65.5	331.1
			88.3	70.0	331.9
			90.2	73.0	332.9
			94.5	82.2	333.2
			96.8	90.0	335.4
			98.8	94.2	336.4
12	A = CH ₃ OCH ₃ B = C ₆ H ₆	10.000	0.0	0.0	352.8
			4.0	15.1	348.2
			15.9	35.3	342.5
			29.8	40.5	341.5
			42.1	43.6	340.8
			53.7	46.6	341.0
			62.9	50.5	341.4
			71.8	54.9	342.0
			79.8	60.6	343.3
			87.2	68.3	344.8
			93.9	78.7	347.4
			100.0	100.0	351.1
13	A = CH ₃ COCH ₃ B = CH ₃ OH	10.133	0.0	0.0	337.7
			4.8	14.0	335.9
			17.6	31.7	333.1
			28.0	42.0	331.3
			40.0	51.6	330.2
			60.0	65.6	329.1
			80.0	80.0	328.6
			90.0	94.0	328.8
			99.0	97.0	329.1
			100.0	100.0	329.5

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x-liquid phase	y-vapour phase	
14	A = CH_3COCH_3 B = CHCl_3	9.760	0.0	0.0	332.9
			7.9	6.0	333.3
			14.3	11.6	334.2
			18.6	16.0	334.8
			26.6	23.5	335.2
			39.4	39.4	335.4
			46.2	52.0	335.0
			53.6	59.8	334.3
			61.8	69.8	333.3
			71.5	79.2	331.9
			77.0	84.8	331.2
			82.1	90.1	330.2
			91.5	95.4	329.0
			100.0	100.0	328.2
15	A = CH_3COCH_3 B = CHCl_3	10.000	0.0	0.0	334.3
			18.6	10.3	336.0
			34.0	31.8	336.8
			46.8	51.5	336.4
			57.8	65.2	335.2
			67.3	75.7	334.0
			75.5	83.2	332.9
			82.7	89.0	331.8
			89.2	93.6	330.8
			94.9	97.3	330.0
			100.0	100.0	329.0
16	A = $\text{C}_3\text{H}_8\text{O}$ B = H_2O	10.133	0.0	0.0	373.0
			1.0	11.0	368.0
			2.0	21.6	365.0
			4.0	32.0	363.5
			6.0	35.1	362.3
			10.0	37.2	361.5
			20.0	39.2	361.1
			30.0	40.4	360.9
			40.0	42.4	360.8
			50.0	45.2	360.9
			60.0	49.2	361.3

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x-liquid phase	y-vapour phase	
16	A = C_3H_8O B = H_2O	10.133	70.0	55.1	362.0
			80.0	64.1	363.5
			85.0	70.4	364.5
			90.0	77.8	365.8
			96.0	90.0	367.0
			100.0	100.0	370.3
17	A = $C_4H_{10}O$ (diethyl ether) B = $C_6H_{12}O_2$ (butyl acetate)	0.668	0.0	0.0	325.6
			18.0	22.5	324.5
			28.2	32.2	324.1
			35.5	36.3	323.8
			37.0	37.0	323.7
			43.5	41.6	323.8
			59.1	50.4	324.2
			76.5	64.5	325.3
			86.8	75.2	326.5
			92.1	83.3	327.7
			100.0	100.0	329.1
18	A = $C_4H_{10}O$ (diethyl ether) B = $C_6H_{12}O_2$ (butyl acetate)	2.200	0.0	0.0	353.6
			16.1	21.0	351.2
			31.3	37.5	349.9
			47.4	47.9	349.4
			61.3	57.8	349.5
			77.7	70.5	350.2
			87.3	80.7	351.3
			100.0	100.0	353.3
19	A = $C_4H_{10}O$ (diethyl ether) B = $C_6H_{12}O_2$ (butyl acetate)	10.133	0.0	0.0	399.0
			21.9	33.4	394.2
			37.2	48.2	391.9
			51.4	58.0	390.9
			66.4	69.2	390.1
			72.2	74.1	389.9
			77.9	78.6	389.8
			84.7	84.4	390.0
			89.6	88.0	390.1
			100.0	100.0	390.5

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x -liquid phase	y -vapour phase	
20	A = CHCl_3 B = CH_3OH	10.100	0.0	0.0	337.9
			2.9	8.3	337.1
			6.3	16.1	335.4
			10.3	24.0	333.7
			15.2	32.3	332.1
			21.2	41.2	330.5
			28.7	48.8	328.9
			38.5	54.2	327.5
			51.8	58.9	326.7
			70.72	67.8	326.7
			84.7	82.3	330.0
			100.0	100.0	334.4
21	A = CCl_4 B = $\text{CH}_3\text{CH}_2\text{OH}$	9.930	0.0	0.0	350.9
			3.2	16.6	347.8
			7.0	26.5	345.4
			11.4	35.4	343.3
			16.6	43.5	341.4
			23.0	49.8	339.6
			31.0	53.6	338.3
			41.1	56.9	337.4
			55.67	59.7	336.9
			63.0	63.0	336.6
			72.9	66.9	337.3
			89.0	84.0	343.0
			100.0	100.0	348.9
22	A = CCl_4 B = $\text{C}_4\text{H}_8\text{O}_2$ (ethyl acetate)	9.140	0.0	0.0	347.1
			0.5	0.8	347.0
			7.3	10.0	346.3
			15.9	20.2	345.8
			28.0	32.4	345.2
			35.2	38.9	344.9
			42.9	45.9	344.7
			51.3	52.8	344.6
			57.2	57.7	344.6
			58.8	48.7	344.6
			61.3	61.0	344.6

(Table continued)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x-liquid phase	y-vapour phase	
22	A = CCl_4 B = $\text{C}_4\text{H}_8\text{O}_2$ (ethyl acetate)	9.140	69.3	67.5	344.8
			79.2	76.5	345.1
			89.4	87.1	345.6
			100.0	100.0	346.4
23	A = $\text{C}_6\text{H}_5\text{CH}_3$ B = <i>iso</i> - $\text{C}_4\text{H}_{10}\text{O}$ (<i>iso</i> -butanol)	10.133	0.0	0.0	381.0
			6.6	13.1	378.2
			11.4	21.8	376.6
			15.0	26.7	375.8
			21.1	33.4	374.9
			33.3	42.1	374.2
			35.5	44.2	374.1
			44.1	48.0	373.8
			55.0	53.6	373.5
			58.8	54.4	373.6
			63.8	57.0	373.4
			68.2	59.8	374.4
			76.2	64.1	374.9
			80.3	67.4	375.5
			84.4	71.2	376.3
			87.0	73.6	376.8
			89.7	77.3	377.7
			96.5	87.0	380.2
			100.0	100.0	383.4
24	A = <i>trans</i> - $\text{C}_2\text{H}_2\text{Cl}_2$ (<i>trans</i> -dichloroethane) B = CH_3OH	10.133	0.0	0.0	337.6
			0.7	5.1	336.4
			2.1	13.8	339.9
			2.8	16.8	333.5
			5.8	30.4	329.5
			11.2	45.2	325.3
			13.4	48.5	324.1
			18.7	53.8	321.1
			24.6	59.3	319.0
			29.4	65.3	317.8
			34.3	68.0	317.3
			43.8	72.8	316.0
			73.7	76.0	315.0
			76.9	76.9	314.9

(Table concluded)

Variant	System	$P \times 10^{-4}$, Pa	Mole percentage of A		T, K
			x-liquid phase	y-vapour phase	
24	A = <i>trans</i> -C ₂ H ₂ Cl ₂ (<i>trans</i> -dichloroethane) B = CH ₃ OH	10.133	88.6	79.0	315.3
			95.5	83.0	316.1
			98.7	90.6	317.8
			99.6	94.4	319.0
			100.0	100.0	321.3
25	A = <i>cis</i> -C ₂ H ₂ Cl ₂ B = CH ₃ OH	10.133	0.0	0.0	337.6
			2.9	8.9	336.3
			4.8	13.7	334.8
			7.0	18.7	333.6
			13.6	33.1	331.0
			16.9	37.1	329.9
			19.6	39.1	329.0
			25.9	45.4	327.5
			31.4	50.4	326.7
			36.5	53.9	326.1
			40.0	55.9	325.6
			42.6	57.6	325.4
			51.3	60.9	325.0
			57.1	63.4	324.8
			65.1	65.1	324.5
			70.5	65.5	324.8
			85.0	70.8	325.3
			91.6	74.0	325.9
			98.6	84.0	328.4
			99.6	87.3	329.3
			99.8	93.9	330.8
			100.0	100.0	333.3

of the liquid phase and y of the saturated vapour is expressed as percentage of substance A. Proceeding from these data, (1) plot the composition of the vapour phase versus that of the liquid phase at a constant pressure; (2) draw the boiling-point diagram of the A-B system; (3) determine the boiling point of a system containing $a\%$ (mol.) A; what is the composition of the first vapour bubble over the system and that of the last drop of the liquid phase? At what temperature will the system stop boiling? (4) determine the composition of the vapour at equilibrium with the liquid phase boiling at temperature T_1 ; (5) in what type of experiment can the com-

position of a liquid binary system be established if the system starts boiling at temperature T_1 , provided the boiling-point diagram of the system is available? (6) determine what component and in what amount can be abstracted from a system containing b kg of substance A and c kg of substance B; (7) determine what component and in what amount is to be added to the system specified in (6) in order to obtain an azeotropic system; (8) determine the amount of substance A, which will be present in the vapour and liquid phases, if 2 kg of a mixture with $a\%$ (mol.) A are heated to temperature T_1 ; and (9) determine the variance of the system at the azeotropic point.

Vari- ant	T_1	a	b	c	Vari- ant	T_1	a	b	c
1	388	55	81	19	14	334.5	55	37.2	62.8
2	393	60	61.2	38.8	15	336	55	37.2	62.8
3	383	65	67.4	32.6	16	365	80	93	7
4	372	50	15.8	84.2	17	325	65	54.2	45.8
5	368	50	19.6	80.4	18	350.5	75	65.5	34.5
6	365	35	68.8	31.2	19	390.25	65	54.2	45.8
7	367	25	6.4	93.6	20	330.3	25	55.5	44.5
8	317	25	30.4	69.6	21	343	25	36.8	63.2
9	333	25	27.1	72.9	22	345.5	25	52.7	47.3
10	331	80	62.2	37.8	23	377	80	83.4	16.6
11	335	10	4.4	56.4	24	320	25	50.5	49.5
12	345	75	64	36	25	339	25	50.5	49.5
13	329.25	60	73	27					

2. Proceeding from the total pressure and composition of the vapour phase at equilibrium with the boiling liquid, stated on p. 246, determine the activity and activity coefficient of component A in the liquid phase at a given composition of the latter and at a given temperature. Use the Clapeyron-Clausius equation and the values given in the handbook to calculate the saturated vapour pressure P_A^0 over component A. Determine the change in the chemical potential during formation of the solution at given values of concentration and temperature.

Variant	System	$P \times 10^{-4}$, Pa	Mole percent- age of A	T , K
1	HNO ₃ -H ₂ O	10.133	53.0	385.0
2	HNO ₃ -C ₂ H ₄ O ₂	10.079	60.0	378.0
3	HF-H ₂ O	10.133	61.7	352.0

(Table concluded)

Variant	System	$P \times 10^{-4}$, Pa	Mole percent- age of A	T, K
4	$\text{H}_2\text{O}-\text{C}_5\text{H}_4\text{O}_2$	10.133	8.0	395.5
5	$\text{H}_2\text{O}-\text{C}_4\text{H}_{10}\text{O}$	10.133	25.7	370.9
6	$\text{H}_2\text{O}-\text{C}_4\text{H}_{10}\text{O}$	10.133	17.2	369.0
7	$\text{H}_2\text{O}-\text{C}_5\text{H}_{12}\text{O}$	10.246	18.9	367.8
8	$\text{CS}_2-\text{C}_3\text{H}_8\text{O}$	10.133	13.4	319.6
9	$\text{CH}_3\text{OH}-\text{CCl}_4$	10.133	3.0	335.0
10	$\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$	9.670	5.9	330.7
11	$\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$	10.133	90.2	332.9
12	$\text{C}_2\text{H}_6\text{O}-\text{C}_6\text{H}_6$	10.000	4.0	348.2
13	$\text{C}_6\text{H}_6\text{O}-\text{CH}_3\text{OH}$	10.133	17.6	333.1
14	$\text{C}_3\text{H}_8\text{O}-\text{CHCl}_3$	9.760	77.0	331.2
15	$\text{C}_3\text{H}_8\text{O}-\text{CHCl}_3$	10.000	18.6	336.0
16	$\text{C}_3\text{H}_8\text{O}-\text{H}_2\text{O}$	10.133	4.0	363.5
17	$\text{C}_4\text{H}_{10}\text{O}-\text{C}_6\text{H}_{12}\text{O}_2$	0.668	28.2	324.1
18	$\text{C}_4\text{H}_{10}\text{O}-\text{C}_6\text{H}_{12}\text{O}_2$	2.200	16.1	351.2
19	$\text{C}_4\text{H}_{10}\text{O}-\text{C}_6\text{H}_{12}\text{O}_2$	10.133	21.9	394.2
20	$\text{CHCl}_3-\text{CH}_3\text{OH}$	10.100	6.3	335.4
21	$\text{CCl}_4-\text{C}_4\text{H}_8\text{O}_2$	9.930	7.0	345.4
22	$\text{CCl}_4-\text{C}_4\text{H}_8\text{O}_2$	9.140	28.0	345.2
23	$\text{C}_7\text{H}_8-\text{C}_4\text{H}_{10}\text{O}$	10.133	11.4	376.6
24	$\text{C}_2\text{H}_2\text{Cl}_2-\text{CH}_3\text{OH}$	10.133	2.8	333.5
25	$\text{C}_2\text{H}_2\text{Cl}_2-\text{CH}_3\text{OH}$	10.133	4.8	334.8

CHAPTER 15

Heterogeneous Equilibrium in Binary Systems
Containing Liquid and Solid Phases

Basic Equations and Symbols

The temperature dependence of solubility of a component in an ideal solution is given by the Schröder equation

$$\log x_i = \frac{\Delta H_{\text{fus}, i}}{2.3026R} \left(\frac{1}{T_{\text{m}, i}} - \frac{1}{T} \right) \quad (15.1)$$

in which x_i is the molar fraction of the solute in a saturated solution (solubility), $\Delta H_{\text{fus}, i}$ is the molar heat of fusion of the solute, $T_{\text{m}, i}$ is the melting point of the pure solute, and T is the temperature of the onset of crystallization of a saturated solution of concentration x_i .

For finitely diluted solutions, the Schröder equation takes the form

$$x_2^{\text{liq}} = \frac{\Delta H_{\text{fus}_1} \Delta T}{RT_{m_1}^2 (1 - K_2)} \quad (15.2)$$

where ΔT is the decrease in the temperature of crystallization of the solution (melt) of concentration x_2^{liq} ;

$$\Delta T = T_{m_1} - T \quad (15.3)$$

T_{m_1} is the melting point of the solvent, ΔH_{fus_1} is the heat of fusion of the solvent, and $K_2 = x_2^s/x_2^{\text{liq}}$, x_2^s being the concentration of the solute in the solid solution and x_2^{liq} being the solute concentration in the liquid solution (melt).

In the case of non-isomorphically crystallizing systems, $x_2^s = 0$ and $K_2 = 0$.

Exercises

1. Proceeding from the cooling curves for a gold-platinum system (Fig. 29a), plot the composition-versus-property curve and determine

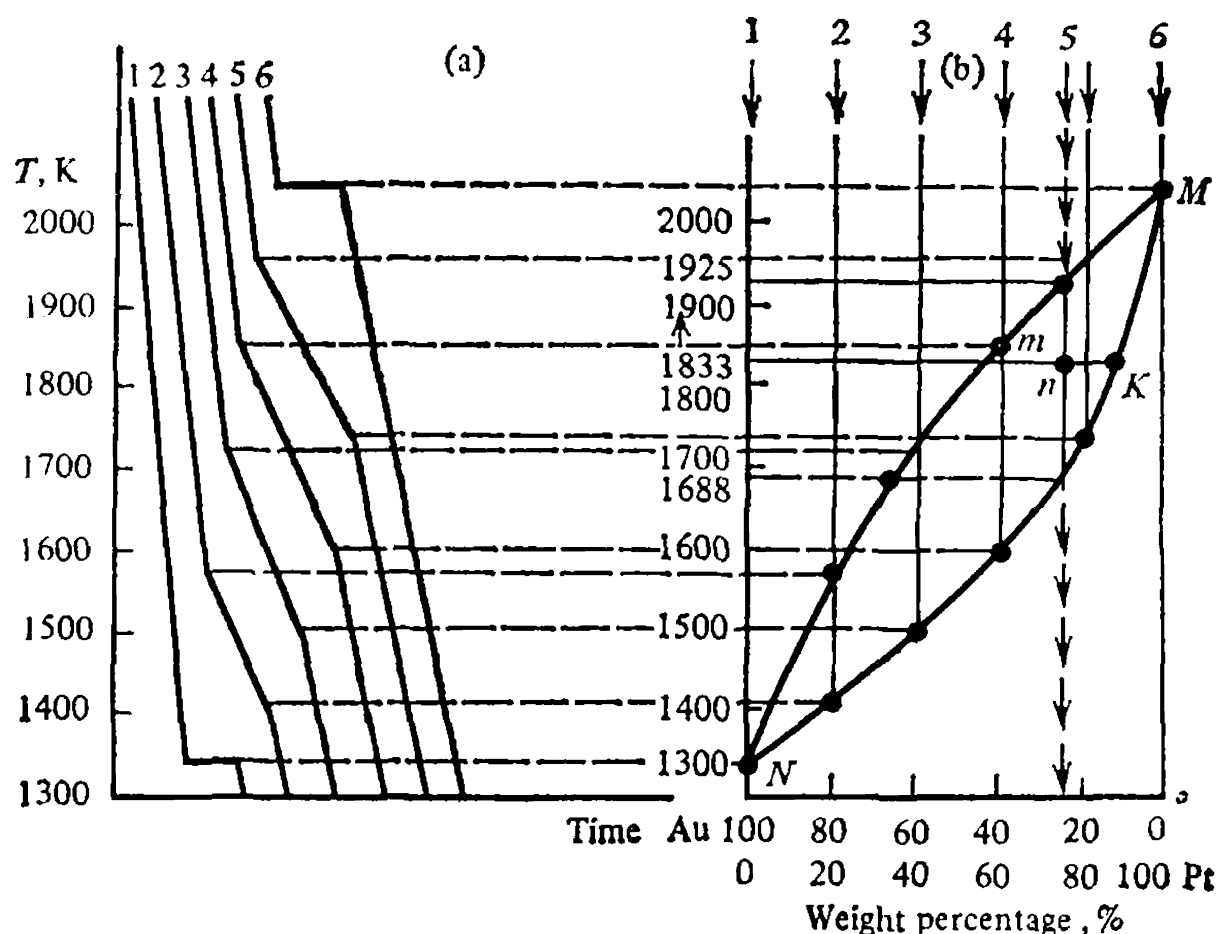


Fig. 29. Cooling curves for an isomorphous Au-Pt system (a) and melting-point diagram for the same system (b)

(1) the temperature at which the melt containing 75% (wt) Pt will start to solidify, (2) the temperature at which the melt will solidify completely, (3) the composition of the first crystals precipitating

into the solid phase, (4) the amounts of gold and platinum in the solid and liquid states when 3 kg of a system with 75% (wt) Pt are cooled down to 1833 K, and (5) the composition of the last drop of the melt.

Solution. Draw the fusion diagram proceeding from the cooling curves (Fig. 29b). Curve 1 corresponds to cooling of pure gold. At 1337 K, the cooling curve flattens over a portion corresponding to the melting point of gold. Pure substances crystallize at a constant temperature. According to Gibbs' phase rule (11.3), the number of components is $K = 1$, and the number of phases is $\Phi = 2$, $n = 1$; since the system is not influenced by pressure, the number of thermodynamic degrees of freedom is $f_{\text{cond}} = 1$.

Curve 2 corresponds to cooling of a system containing 20% Pt. At 1567 K, the cooling rate starts decreasing as a result of a heat-releasing process which is crystallization of the solid solution. The heat released during crystallization is the reason why the system cooling rate decreases. At 1405 K, an increase in the cooling rate is observed on the same curve. This temperature marks the point where the crystallization of the solid solution is complete and the subsequent cooling is not accompanied by heat release. The solid solution is steadily cooled from now on. Plot the temperatures corresponding to the onset (1567 K) and end (1405 K) of crystallization of a melt with 20% Pt on the Y axis. Similarly, plot the temperatures of onset and end of crystallization for melts with 40, 60, and 80% Pt. Connecting all points corresponding to the onset of crystallization gives the liquidus curve, while doing the same with the points corresponding to the end of crystallization gives the solidus curve. The two curves converge at the crystallization points of the pure components Pt and Au.

Thus, above the NmM curve all systems are in the liquid state with one phase, two components, and two conditional thermodynamic degrees of freedom. Even if the composition and temperature are varied within reasonable limits, neither the number nor the kind of phases will change. Below the NKM curve all systems are in the state of a solid solution whose composition may change continuously. There is one phase, two components, and two conditional thermodynamic degrees of freedom. Between the NmM and NKM curves all systems are heterogeneous. Two phases are at equilibrium, namely, the solid solution whose composition can be determined from the NKM curve and the melt whose composition can be determined from the NmM curve. There are two phases, two components, $n = 1$, and $f_{\text{cond}} = 1$. The composition may be altered.

The crystallization of a system with 75% Pt starts at 1925 K and ends at 1688 K. The composition of the coexisting phases can be determined from the points of intersection of the isotherm with the NmM and NKM curves. The first crystal will contain 92% Pt.

At 1833 K, the solid solution and melt are at equilibrium. The weight of the solid solution relates to that of the liquid melt, according to the lever principle (14.4), as arm mn relates to arm nK . If the total weight is 3 kg, denote the weight of the solid solution by x and that of the liquid melt by $3 - x$. Measure the lengths of the arms or calculate the compositions as percentage:

$$\frac{x}{3-x} = \frac{75-57}{88-75} = 0.14, \quad y = 1.75 \text{ kg}$$

The solid solution weighs 1.75 kg, and the liquid melt weighs 1.25 kg. The solid solution will contain $1.75 \times 0.88 = 1.535$ kg of platinum and $1.75 \times 0.12 = 0.215$ kg of gold. In the melt, there is $1.25 \times 0.57 = 0.712$ kg of platinum and $1.25 \times 0.43 = 0.538$ kg of gold. To make sure that the obtained values are correct, add up the weights of platinum and gold:

weight of Au	$0.215 + 0.538 = 0.753 \text{ kg}$
weight of Pt	$1.535 + 0.712 = 2.247 \text{ kg}$
Total	3.000 kg

$$\frac{0.753}{3.000} = 0.25, \quad \text{or} \quad 25\%, \quad \frac{2.247}{3.000} = 0.75, \quad \text{or} \quad 75\%$$

The composition of the last drop of the melt is given by the intersection of the isotherm of end of crystallization with the NKM curve. The last drop of the melt will contain 34.5% Pt. The crystallization of the melt with 75% Pt is shown by arrows in Fig. 29b.

2. Determine the heat of fusion of platinum proceeding from the fusion diagram for the Pt-Au system (Fig. 29).

Solution. To calculate $\Delta H_{\text{fus, Pt}}$ use Eq. (15.2). Determine the molar fraction of platinum in a melt containing 25% Au:

$$x_{\text{Pt}}^{\text{liq}} = \frac{25/197.0}{(25/197.0) + (75/195.1)} = 0.247$$

$$x_{\text{Pt}}^{\text{s}} = \frac{8/197.0}{(8/197.0) + (92/195.0)} = 0.085$$

$$K_{\text{Pt}} = 0.085/0.247 = 0.345, \quad \Delta T = 2054 - 1833 = 221 \text{ K}$$

$$\Delta H_{\text{fus, Pt}} = 247 \frac{8.3143 \times 2054^2}{221} (1 - 0.345) = 25.679 \times 10^3 \text{ J/mole}$$

The result is approximate because the solution is infinitely diluted.

3. Proceeding from the cooling curves for an aluminium-silicon system (Fig. 30a), draw the fusion diagram and determine (1) the temperature at which a system containing 60% Si will start to crystallize, (2) the substance that will crystallize from the melt with 60% Si, (3) the amount of the solid phase at 1073 K if the total weight of the system with 60% Si is 2 kg, (4) the temperature

at which the crystallization of the system will end, and (5) the composition of the last drop of the liquid melt.

Solution. Draw the fusion diagram, proceeding from the cooling curves (Fig. 30a), with composition being plotted versus melting point (Fig. 30b). When pure silicon is cooled (cooling curve *I*), the cooling curve flattens over a portion corresponding to 1693 K,

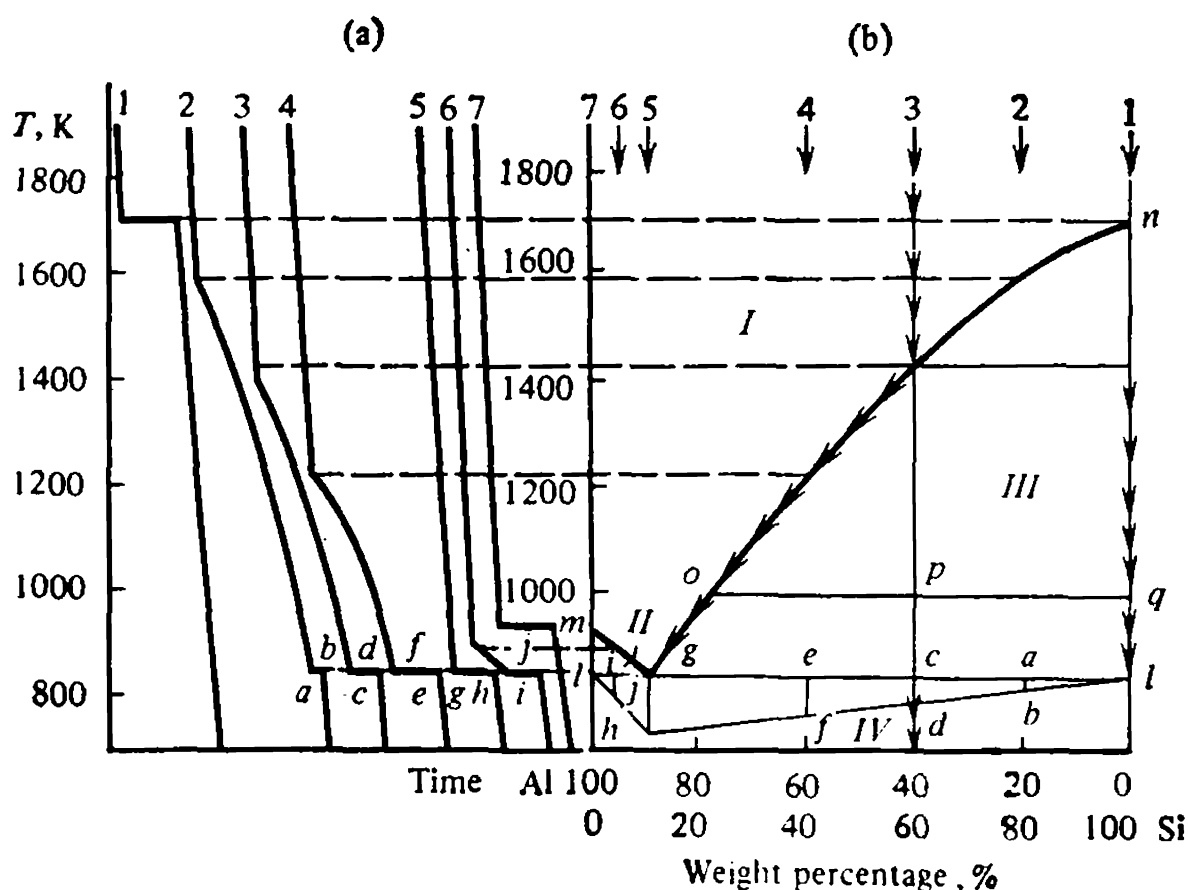


Fig. 30. Cooling curves for a nonisomorphic Al-Si system (a), and melting-point diagram for the same system (b)

which is due to release of the latent heat of crystallization of silicon at its melting point. Plot this temperature on the ordinate (Fig. 30b) corresponding to pure silicon.

At 1593 K, the cooling curve for a system with 80% Si (curve 2) shows a decrease in the cooling rate. At this temperature, pure silicon will start to crystallize from the melt; since the Al-Si system is nonisomorphic, the solubility of components in the solid state is nil (or rather negligibly low). When silicon passes into the solid phase, the liquid phase becomes richer in aluminium, and the melting point of the system goes down. Cooling curve 2 flattens at a temperature of 845 K (portion *ab*). At this temperature, the entire system becomes solid. The flattening of the curve is caused by simultaneous crystallization of aluminium and silicon from the melt. Here the compositions of the liquid and solid phases do not change. For this reason, the melting and crystallization points remain invariable.

When a system containing 40% Si is cooled (curve 4), the cooling rate changes already at 1219 K, and the flattening of the curve is observed at the same temperature as during cooling of the melt with 80% Si, i.e. at 845 K. At 1219 K silicon starts crystallizing from the melt, the aluminium content in the latter increases, the crystallization point is lowered, and the eutectic mixture undergoes crystallization at 845 K. The length of the plateau on the cooling curve is proportional to the heat released during crystallization of the eutectic mixture. Since the composition of the latter is constant, the length of the plateau is proportional to the amount of the eutectic mixture undergoing crystallization. If the same amount of melts with different compositions is cooled, the eutectic mixture will differ in quantity, which is why the plateau on the cooling curves varies in length.

If a system containing 10% Si is cooled (curve 5), no change in the cooling rate is observed on the curve which only flattens at 845 K. The composition containing 10% Si and 90% Al is eutectic. The plateau on cooling curve 5 is the longest. Cooling of pure aluminium entails flattening of the curve (curve 7) at 932 K which is the melting point of aluminium.

As the fusion diagram is completed, incorporating all cooling curves, we obtain two curves mz and nz and horizontal straight line kl . The three lines intersect at the eutectic point where the melt is saturated both with silicon and with aluminium. Above the mz and nz curves, in region *I*, all systems are homogeneous and there is only one, liquid, phase and two thermodynamic degrees of freedom. In region *II*, the systems are heterogeneous with aluminium crystals being at equilibrium with the melt whose composition is determined from the mz curve. In region *III*, all systems are heterogeneous, too. Here, silicon crystals are at equilibrium with the melt whose composition is determined from the nz curve. The systems in regions *II* and *III* have one thermodynamic degree of freedom each. In region *IV*, all systems are in the solid state, heterogeneous, and have two solid phases—crystals of aluminium and silicon. There is one thermodynamic degree of freedom. In the state of equilibrium at point z are aluminium crystals, silicon crystals, and the melt; the system is heterogeneous with three phases and zero thermodynamic degrees of freedom.

Since the length of the plateau corresponding to crystallization of the eutectic mixture on the cooling curves is proportional to the amount of the eutectic mixture, this proportionality can be used to determine the concentration of the components at the eutectic point. To this end, draw a Tammann triangle. Plot the lengths of plateaus ab , cd , ef , gh , and ij (Fig. 30a) downward vertically from the eutectic isotherm at points corresponding to the composition of the systems (Fig. 30b), and the intersection of the lines drawn

through points l , b , d , f , h and k , j , h gives the composition of the eutectic mixture.

The cooling of the system with 60% Si is indicated by arrows on the fusion diagram (Fig. 30b). The system starts crystallizing at 1408 K. Silicon passes into the solid phase, and the melt becomes enriched with aluminium. As soon as the system is cooled down to 1000 K, a certain amount of silicon forms crystals. To determine the amounts of the liquid and solid phases at equilibrium use the lever principle. The weight of silicon crystals relates to that of the liquid phase as the length of arm op relates to that of arm pq . If the weight of the system is 2 kg, then

$$\frac{x}{2-x} = \frac{60-24}{100-60} = 0.9, \quad x = 0.95 \text{ kg}$$

The weight of silicon crystals is 0.95 kg and that of the melt with 24% Si is 1.05 kg. The crystallization of the system containing 60% Si will be over at the eutectic temperature of 845 K. The composition of the last drop of the melt corresponds to the eutectic one, i.e. 10% Si.

4. Determine the heat of fusion, ΔH_{fus} , of silicon with the aid of the fusion diagram for the aluminium-silicon system (Fig. 30b).

Solution. The Al-Si system is nonisomorphous. For such a system, K in Eq. (15.2) is zero. The temperature of the onset of crystallization of a system with 20% Al is 1593 K. The crystallization point of pure silicon is 1693 K. The decrease in the crystallization point is

$$\Delta T = 1693 - 1593 = 100 \text{ K}$$

Determine the molar fraction of aluminium in the system:

$$x_{\text{Al}} = \frac{20/27}{20/27 + 80/28} = 0.206$$

According to Eq. (15.2),

$$\Delta H_{\text{fus}} = \frac{0.206 \times 8.3143 \times 1693^2}{100} = 49.091 \times 10^3 \text{ J/mole}$$

This result is approximate because the silicon concentration is sufficiently high.

5. Analyse the fusion diagram of a system with finite solubility of components B and A in the solid state (Fig. 31). Follow the change in the phase state during cooling of a system with 90% A.

Solution. Consider the phase state of the system characterized by points in different parts of the diagram. In region I , the systems are homogeneous with one liquid phase. With this one phase and two components the number f of thermodynamic degrees of freedom under conditions where pressure does not affect the phase equilibrium

($n = 1$) will be

$$f_{\text{cond}} = K - \Phi + n = 2 - 1 + 1 = 2$$

It is possible to change both the composition and the temperature. In regions *II* and *III*, the systems are heterogeneous. Two phases, the solid solution and the melt, are at equilibrium. The composition of the liquid melt is determined from the upper liquidus curve, and that of the solid solution is determined from the lower solidus curve:

$$f_{\text{cond}} = 2 - 2 + 1 = 1$$

Only the composition of the system can be changed (within reasonable limits). In regions *IV* and *V*, the systems are homogeneous with one phase which is a solid solution. In region *IV*, we have a solution of A in B, and in region *V*, a solution of B in A; $f_{\text{cond}} = 2$.

The system in region *VI* is heterogeneous with two solid phases at equilibrium and $f_{\text{cond}} = 1$. It should be borne in mind, however, that it takes much time for equilibrium to be established in the solid phases, therefore the curves of compositions of the solid solutions are usually drawn as dashed lines in fusion diagrams. Two solid phases, two solid solutions, and a liquid melt converge at point *E*. The system is heterogeneous with three phases and $f_{\text{cond}} = 0$.

Now follow the course taken by the process of cooling of a system with 90% A and change in the phase state of the system during cooling. When the system is cooled to temperature T_1 , there is only one phase—liquid melt. At T_1 , there emerges the first crystal of a solid solution whose composition is determined by point *c*. It is component A that passes predominantly from the melt into the solid phase, and the solid solution becomes richer in component A than the melt. Consequently, the melt composition varies along the *ab* curve. Not only the composition of the liquid melt changes but also the crystallization point and the composition of the solid solution do. The composition of the latter varies along the *cd* curve. The crystallization is over when the composition of the solid solution corresponds to that of the liquid melt of the system in the initial

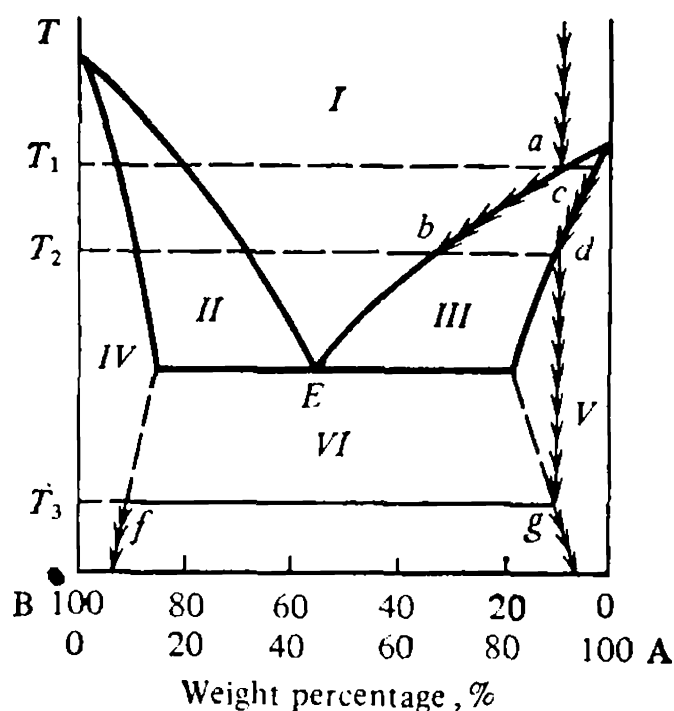


Fig. 31. Melting-point diagram for a binary system with limited solubility of components in the solid state

state at temperature T_2 . The composition of the last drop of the liquid melt is determined by point b . Then cooling of the solid solution takes place. At temperature T_3 , the second solid phase appears, its composition being determined by point f . As cooling of the system continues, the compositions of the solid solutions change as indicated by arrows in the diagram. The change in the composition of the solid solutions is extremely slow. The curves in the fusion diagram correspond to equilibrium concentrations.

6. Analyse the phase state of a nonisomorphic system whose components form a stable chemical compound. Its fusion diagram is shown in Fig. 32. Analyse the process of heating of two binary systems: $A-A_xB_y$ and A_xB_y-B .

Solution. This fusion diagram may be regarded as two independent diagrams for two binary systems: $A-A_xB_y$ and A_xB_y-B . First, cover the part of the diagram that corresponds to the A_xB_y-B system with a piece of paper and mentally compare it with the fusion diagram for a nonisomorphic system which is a simple eutectic (see Fig. 30b). Repeat the procedure covering the part of the diagram that corresponds to the $A-A_xB_y$ system.

In region *I* (Fig. 32), all systems are homogeneous with one phase which is liquid melt and $f_{\text{cond}} = 2$. In region *II*, the systems are heterogeneous. Two phases are at equilibrium, i.e. melt and crystals of component *A*; $f_{\text{cond}} = 1$. In regions *III* and *IV*, the systems are heterogeneous with two phases at equilibrium—liquid melt and crystals of component A_xB_y ; $f_{\text{cond}} = 1$. The systems in region *V* are heterogeneous with two phases at equilibrium—liquid melt and crystals of component *B*; $f_{\text{cond}} = 1$. In region *VI*, the systems are heterogeneous with two phases at equilibrium—crystals of *A* and those of A_xB_y ; $f_{\text{cond}} = 1$. Finally, in region *VII*, the systems are heterogeneous with two solid phases at equilibrium—crystals of A_xB_y and those of *B*; $f_{\text{cond}} = 1$. At points E_1 and E_2 the systems are heterogeneous. Three phases—two solid and one liquid—are at equilibrium; $f_{\text{cond}} = 0$.

Now analyse the process of heating of the system of composition a_1 . When the system is heated to temperature T_1 , no change in the

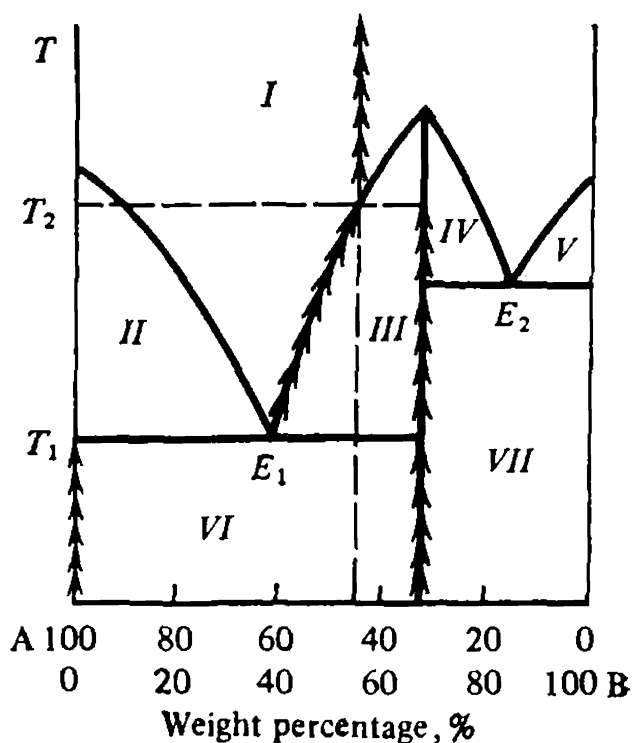


Fig. 32. Melting-point diagram for a nonisomorphic binary system; the substances form a stable chemical compound

phase state is observed. The heating of crystals of A and A_xB_y is indicated in the diagram by the arrows along the Y axes of A and A_xB_y . At T_1 , the system starts to melt. The heating curve must be flattened at that point because of melting of the eutectic mixture. The compositions of the solid and liquid phases remain the same along with temperature until the eutectic mixture melts completely. Next, crystals of A_xB_y melt, and the composition of the liquid phase changes, while that of the solid phase does not (A_xB_y). The change in the composition of the liquid phase affects the melting point.

At temperature T_2 , the composition of the liquid phase becomes a_1 , that is, the same as in the initial state of the system. At this temperature, the last crystal of A_xB_y melts, and the subsequent heating of the liquid melt involves no further changes in the phase state of the system.

The maximum corresponding to the melting point of the chemical compound is indicative of its stability at the melting point. Shifting of the equilibrium of the reaction $A_xB_y \rightleftharpoons xA + yB$ to the right lowers the melting point, and the maximum in the fusion diagram loses its sharpness. Conversely, if the equilibrium is shifted towards formation of the compound, the maximum in the fusion diagram becomes even sharper.

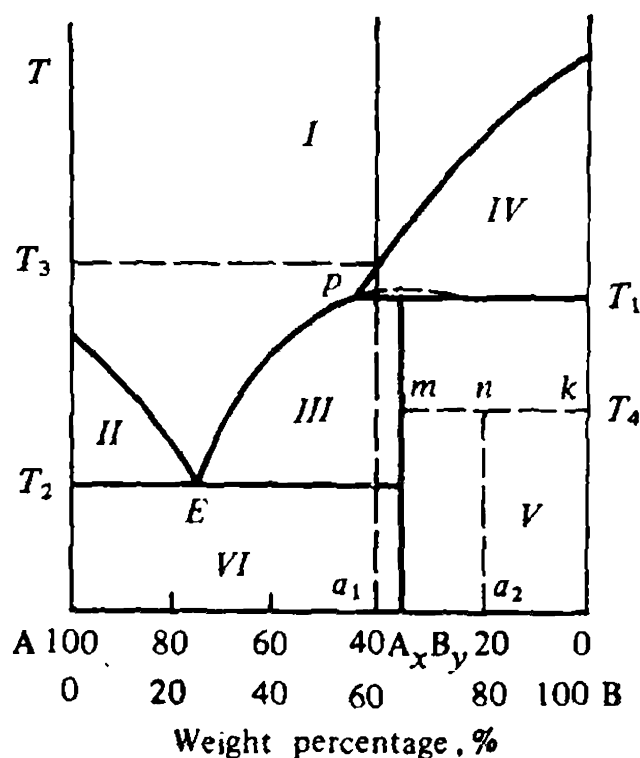


Fig. 33. Melting-point diagram for a nonisomorphous binary system; the substances form an unstable chemical compound

7. Analyse the phase state of a system comprising two nonisomorphically crystallizing components which form an unstable chemical compound (Fig. 33). Follow the change in the phase state of the system during its heating.

Solution. Determine first the phase states of the systems in different parts of the diagram. In region I, all systems are homogeneous with one liquid phase which is the melt; $f_{\text{cond}} = 2$. In region II, the systems are heterogeneous with crystals of component A at equilibrium with the melt; $f_{\text{cond}} = 1$. All systems are heterogeneous in region III. The melt and crystals of the unstable compound A_xB_y are at equilibrium, and $f_{\text{cond}} = 1$. In region IV, the systems are heterogeneous with two solid phases at equilibrium—crystals of B and the melt; $f_{\text{cond}} = 1$. In region V, all systems are heterogeneous with two phases at equilibrium—crystals of B and those of com-

pound A_xB_y . At temperatures below T_1 , the compound becomes stable; $f_{\text{cond}} = 1$. In region VI, all systems are heterogeneous, too. Crystals of A and A_xB_y are at equilibrium; $f_{\text{cond}} = 1$. Three phases coexist at point E, including crystals of A, those of A_xB_y , and the melt; $f_{\text{cond}} = 0$. At point p, three phases are at equilibrium—crystals of B, those of compound A_xB_y which becomes stable at the melting point T_1 , and the melt; $f_{\text{cond}} = 0$.

What happens during heating of a system having composition a_1 ? Up to temperature T_2 the system is in a crystalline state. The crystals of A are at equilibrium with those of compound A_xB_y . At T_2 , the eutectic mixture of composition e starts melting. The compositions of the liquid and solid phases remain invariable until the eutectic mixture melts completely. Consequently, the temperature on the cooling curve does not change. Then, crystals of A_xB_y start to melt, and the composition of the liquid melt changes, while that of the solid phase remains unchanged. At temperature T_1 , the chemical compound becomes unstable. It dissociates into crystals of B and the melt. Since the system becomes nonvariant at T_1 , the heating curve flattens. After the last crystal of A_xB_y disappears, crystals of component B start to melt. The melt composition starts changing again along with the melting point of the system. At temperature T_3 , the composition of the melt becomes a_1 as in the initial state of the system. At this temperature, the last crystal of B disappears, the system becomes homogeneous, and its phase state is not affected by further heating. The heating process and the associated change in the phase state of the system are indicated by arrows in the fusion diagram.

8. Determine the phase state of a system and the weight ratio of its phases if 1 kg of the system having composition a_2 (Fig. 33) is heated to temperature T_4 . Substances A and B are elements with atomic weights 197 and 121.8, respectively. The unstable compound AB_3 contains 80% B (composition corresponding to point a_2).

Solution. The system is heterogeneous. It consists of crystals of the chemical compound and those of component B. To determine the weight ratio of the solid phases use the lever principle. But first determine the percentage content of AB_3 :

$$w_{AB_3} = 3 \times 121.8 / (197.0 + 3 \times 121.8) \times 100 = 64.97\% \text{ B}$$

According to the lever principle:

$$m_B / m_{AB_3} = nk / mn = (100 - 80) / (80 - 64.97) = 1.33$$

Since the total weight of the system is 1 kg, this ratio takes the following form:

$$\frac{x}{1-x} = 1.33, \quad m_s = x = \frac{1.33}{2.33} = 0.57 \text{ kg}, \quad m_{AB_3} = 0.43 \text{ kg}$$

Problems

1. Proceeding from the characteristic points on the cooling curves, draw the fusion diagram for a copper-nickel system:

Ni, %	0	20	40	60	80	100
Temperature of onset of crystallization, K	1373	1467	1554	1627	1683	1728
Temperature of end of crystallization, K	1373	1406	1467	1543	1629	1728

Mark the following with points in the fusion diagram: *a*, pure solid copper at equilibrium with the copper melt; *b*, liquid melt containing 45% Ni at equilibrium with the solid solution; *c*, solid solution containing 65% Ni at equilibrium with the liquid melt, and *d*, liquid melt containing 50% Ni at 1670 K.

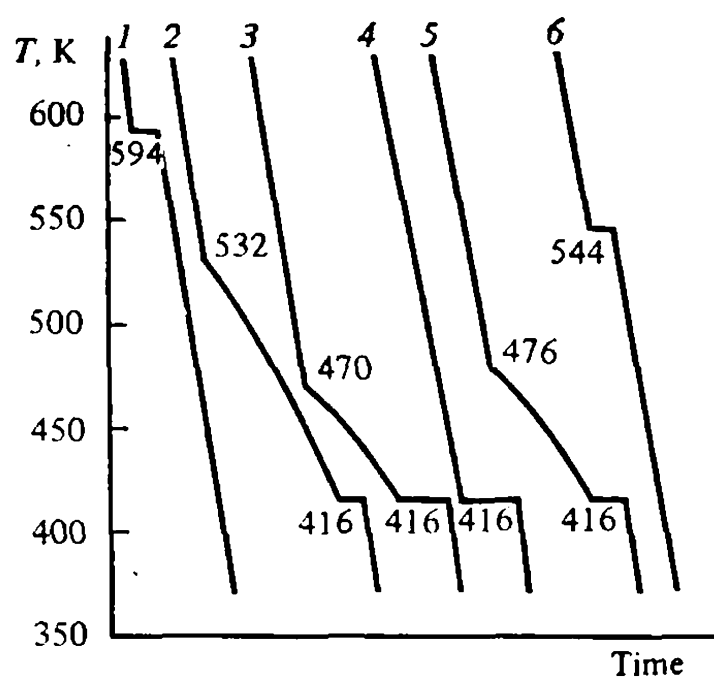


Fig. 34. Cooling curves for a Cd-Bi system:
1—0% Bi; 2—20% Bi; 3—40% Bi; 4—60% Bi;
5—80% Bi; 6—100% Bi

Determine the following for a system containing 30% Ni: the temperature of the onset of crystallization, the composition of the first crystal of the solid solution, the amounts of Ni in the liquid and solid states when 0.24 kg of the system with 30% Ni is cooled down to 1470 K, the temperature of crystallization of the last drop of the liquid melt, and the composition of the last drop of the liquid melt.

2. Draw the composition-versus-melting point diagram for a silver chloride-sodium chloride system, proceeding from the characteristic points on the cooling curves:

Mole percentage of AgCl	0	20	40	60	80	100
Temperature of onset of crystallization, K	1073	1004	941	869	788	728
Temperature of end of crystallization, K	1073	952	848	775	742	728

Mark the following states of the system with points on the diagram: *a*, pure solid silver chloride at equilibrium with the silver chloride melt; *b*, liquid melt with 55% mol. AgCl at 1000 K; *c*, liquid melt with 70% mol. AgCl at equilibrium with the solid solution; *d*, solid solution with 45% mol. AgCl at equilibrium with the liquid melt; and *e*, solid solution with 30% mol. AgCl at 750 K.

3. Proceeding from the cooling curves of a cadmium-bismuth system (Fig. 34) draw the fusion diagram. Mark the following states of the system with points on the diagram: *a*, pure bismuth at equilibrium with the bismuth melt; *b*, liquid melt with 30% Cd at 573 K; *c*, melt with 15% Cd at equilibrium with bismuth crystals; *d*, equilibrium system consisting of solid cadmium and a melt with $\frac{4}{5}$ Cd

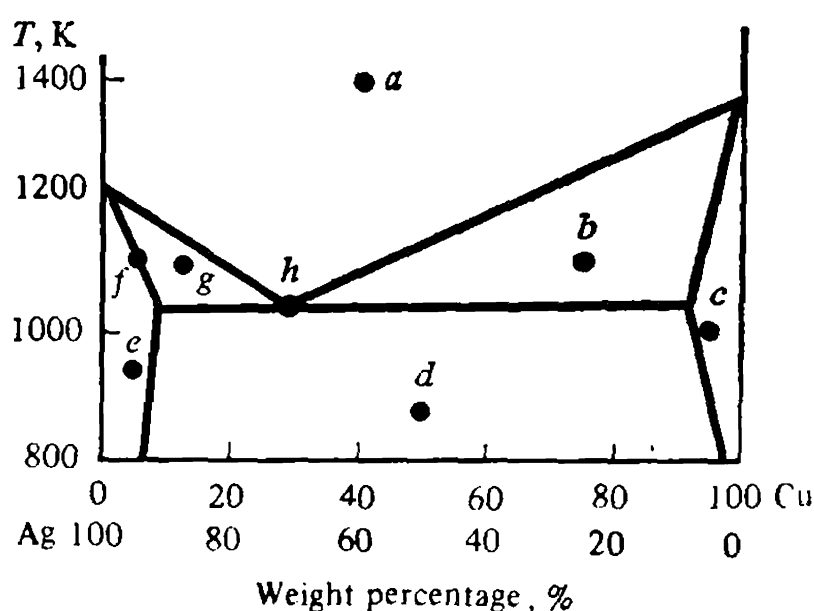


Fig. 35. Melting-point diagram for a binary Ag-Cu system with limited solubility of components in the solid state

and $\frac{1}{5}$ Bi; and *e*, liquid melt containing both metals at equilibrium with solid Cd and Bi.

4. Proceeding from the characteristic points on the cooling curves, draw the fusion diagram for a silver chloride-potassium chloride system:

AgCl, %	0	20	40	60	80	100
Temperature of onset of crystallization, K	1055	958	837	688	630.6	728
Temperature of end of crystallization, K	1055	584	584	584	584	728

Determine the amount of potassium chloride to be added to 1.7 kg of silver chloride in order to lower the initial melting point down to 650 K.

5. Determine, from the fusion diagram of a silver-copper system (Fig. 35), the phase states of the systems marked with points *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h*.

6. Proceeding from the characteristic points on the cooling curves, draw the fusion diagram for a sodium iodide-sodium fluoride system on the basis of the values given in the handbook. What will happen to a solid system containing 0.4 kg NaF and 0.6 kg NaI if it is heated to 670, 899, 950, 1033, and 1200 K?

7. Draw the phase diagram of a phenol-water system, proceeding from the weight percentage of the phases at equilibrium:

(1) water is saturated with phenol to concentration c_1 , and phenol is saturated with water to concentration c_2 :

T, K	280	300	320	330	335	338	341.8
$c_1, \%$	7.9	8.8	11.4	15.5	18.5	22.0	35.9
$c_2, \%$	75.1	70.5	64.0	58.3	54.0	49.5	35.9

(2) solid phenol is at equilibrium with the solution:

T, K	280	290	300	314
$c, \%$	84.0	91.5	95.3	100

The first invariant point is near 272.1 K: ice, phenol, solution. The second invariant point is at 274.5 K: phenol, two solutions. Explain the resulting diagram. Determine the phase state of the systems in every part of the diagram. Define the composition and number of phases in a mixture containing 0.03 kg of phenol and 0.07 kg of water at 300 K. Mark the following with points: *a*, homogeneous solution containing 80% phenol at 320 K; *b*, system with 50% phenol, separable into two immiscible solutions with 9.5 and 63.0% phenol, respectively; and *c*, homogeneous solution containing 5% phenol at 320 K. What will happen in each of the above systems if phenol is slowly added to them? The solutions with 20% phenol in one and 60% phenol in the other have a temperature of 340 K. Down to what temperature must each solution be cooled for the system to separate?

8. Determine the number of conditional thermodynamic degrees of freedom for systems at a given temperature and composition. For their fusion diagrams, see the handbook.

System	AgCl-NaCl	AgCl-NaCl	AgCl-NaCl	Cu-Ni	Cu-Ni
T, K	1073	873	—	1473	
Composition, %	50	50	—	30	
Corresponding point on the diagram			<i>a</i>		<i>a</i>
System	CaCl ₂ -CsCl		CuCl-KCl		
T, K					
Composition, %					
Corresponding point on the diagram	<i>d</i>		<i>d</i>		

9. Proceeding from the fusion diagram of a CaCl₂-CsCl system, given in the handbook, determine the amounts of the solid and liquid phases if a system with 60% mol. CsCl is heated to 1073 K. The total weight of the system is 2 kg. Determine the weight of CaCl₂ and CsCl in the liquid and solid phases if 2 kg of the system with 60% mol. CsCl are heated to 1073 K. Calculate the amount of the

Variant	Systems	Mole percent- age of A	Temperature of onset of crystal- lization, K	Mole percent- age of A	Temperature of onset of crystal- lization, K
1	A = KCl B = SnCl ₂	0	512	40	460
		5	507	45	481
		10	496	50	497
		15	479	52.5	583
		20	477	55	658
		25	481	70	853
		30	478	80	952
		35	473	100	1050
2	A = KCl B = PbCl ₂	0	769	45	693
		10	748	50	703
		20	713	55	733
		25	701	65	811
		30	710	75	893
		33.5	713	90	1003
		40	707	100	1048
3	A = KCl B = MnCl ₂	0	923	50	769
		8	895	60	731
		15	865	65	705
		25	715	66	701
		34	745	75	705
		36	722	85	925
		38	735	100	1047
		40	747		
4	A = Li ₂ CO ₃ B = K ₂ CO ₃	0	1133	50	788
		9	1055	54.5	778
		20	955	62	765
		33	765	66.6	798
		39.5	773	83.5	911
		44.2	778	100	983
5	A = MgSO ₄ B = Cs ₂ SO ₄	0	1294	55	1048
		10	1241	60	1053
		20	1193	63	1098
		30	1116	65	1113
		40	1013	70	1163
		45	953	80	1238
		47	969	90	1323
		50	999	100	1397

(Table continued)

Variant	Systems	Mole percent- age of A	Temperature of onset of crystal- lization, K	Mole percent- age of A	Temperature of onset of crystal- lization, K
6	A = Li_2SO_4 B = Cs_2SO_4	0	1293	65	983
		10	1216	75.5	903
		20	1113	77.5	906
		25	1063	80	910
		31	953	85	905
		35	963	89.5	893
		45	1003	90	910
		50	1011	95	1055
		55	1007	100	1129
7	A = KI B = CdI_2	0	658	53	504
		10	643	55	515
		30	696	60	575
		45	520	65	656
		47	470	80	833
		49	468	100	951
8	A = CsCl B = CsCl_2	0	1147	50	1180
		10	1124	60	1158
		15	1089	70	1071
		20	1059	80	877
		25	1102	85	862
		35	1155	95	875.8
		40	1166	100	876.8
9	A = RbCl B = SrCl_2	0	1147	55	969
		10	1089	65	896
		20	1004	70	827
		30	906	75	853
		40	964	80	879
		45	975	90	960
		50	978	100	999
10	A = KCl B = CaCl_2	0	1043	40	1027
		5	1023	45	1015
		10	978	55	961
		18.5	911	67	873
		20	828	70	899

(Table continued)

Variant	Systems	Mole percent- age of A	Temperature of onset of crystal- lization, K	Mole percent- age of A	Temperature of onset of crystal- lization, K
10	A = KCl B = CaCl ₂	25	980	90	1021
		35	1022	100	1049
11	A = CuCl B = CsCl	0	912	65	542
		10	868	66.6	547
		20	814	70	541
		35	645	75	521
		45	571	80	541
		50	549	90	623
		60	533	100	695
12	A = CdCl ₂ B = TlCl	0	702	50	699
		10	656	57.5	697
		20	604	67.5	673
		28	572	80	754
		30	589	85	777
		36.5	645	95	823
		47	694	100	841
13	A = SrBr ₂ B = KBr	0	1003	57	832
		10	972	66.7	847
		25	872	75	843
		29	829	82	835
		33.3	832	85	851
		40	826	95	897
		50	807	100	916
14	A = InCl ₃ B = NaCl	0	1073	53	983
		13.3	1052	61.6	753
		22.2	1033	66.8	680
		35.8	989	74.6	641
		37.6	975	80.6	622
		40	983	81.6	642
		47	999	84.8	697
		50.6	1003	100	859
15	A = FeCl ₃ B = TlCl	0	702	35	525
		10	658	37	506
		22	598	45	533

(Table continued)

Variant	Systems	Mole percent- age of A	Temperature of onset of crystal- lization, K	Mole percent- age of A	Temperature of onset of crystal- lization, K
15	A = FeCl_2 B = TiCl_3	26	535	52	553
		29	549	62	572
		33	563	100	575
16	A = Na_2S B = KI	0	1121	23.8	1212
		4.9	1099	26	1224
		9.2	1060	30.3	1289
		13.4	1120	37.9	1359
		15.2	1141	46.7	1397
		18.4	1168	50.5	1403
		21.8	1193	58	1391
	A = KI B = FeCl_3	0	685	45	618
		10	668	50	622
		20	640	55	651
		25	622	60	695
		30	579	70	773
		31	594	80	858
		35	603	90	914
		40	610	100	959
18	A = NaNO_2 B = LiH	0	825	50	768
		5	813	54	773
		20	772	66.6	803
		30	736	85	865
		34	720	100	916
		50	744		
19	A = LiNO_3 B = RbNO_3	0	585	50	464
		10	535.5	60	457.6
		20	489	65	449
		22	479	70	567
		32.5	424	80	598
		36	438	90	519.5
		40	449.5	100	527
20	A = MgCl_2 B = TlCl	0	708	50	767
		5	698	66.6	796
		15	682	75	658
		28	635	90	950
		33.3	685	100	991

(Table concluded)

Variant	Systems	Mole percent- age of A	Temperature of onset of crystal- lization, K	Mole percent- age of A	Temperature of onset of crystal- lization, K
21	A = MgCl_2 B = RbCl	0	991	36.2	759
		17.5	868	37.5	784
		22.7	800	43.8	816
		23.7	764	50	823
		25.9	746	58.1	809
		28	736	65	783
		29	732	68.3	821
		30.4	743	78.7	898
		33.1	749	100	984
		33.5	745		
22	A = MnCl_2 B = RbCl	0	999	45	793
		15	879	50	799
		22	813	55	797
		27	749	65	755
		30	741	68	733
		32	733	70	743
		35	713	80	803
		40	767	100	923
23	A = MgSO_4 B = K_2SO_4	0	1349	63.9	1200
		10	1308	66.8	1203
		20	1236	71	1193
		30	1123	75.3	1177
		40	1019	82.2	1247
		50	1103	100	1397
24	A = PbCl_2 B = TlCl	0	708	50	680
		10	679	60	705
		15.5	661	66.6	708
		20	675	70	707
		25	680	75	700
		30	676	80	720
		36.5	650	90	752
		40	658	100	773
25	A = NaCl B = ZnCl_2	0	595	35	623
		5	589	46	683
		10	577	52.5	769
		15	573	58	813
		25	543	67.7	882
		27	535	100	1073
		30	569		

component to be added to the system for it to undergo isothermal melting.

10. Represent the cooling curves for a CuCl-KCl system proceeding from the fusion diagrams given in the handbook, if the mole percentage of CuCl is 0, 20, 40, 60, 80, and 100.

Multivariant Problem

Proceeding from the temperature of onset of crystallization of a binary system: (1) draw the phase (fusion) diagram for an A-B system; (2) mark the following with points: *I*, liquid melt with $a\%$ A at temperature T_1 ; *II*, melt with $a\%$ A at equilibrium with the crystals of the chemical compound; *III*, system containing solid substance A at equilibrium with a melt containing $b\%$ A; *IV*, equilibrium of the phases having the same composition; and *V*, equilibrium of three

Vari- ant	T_1 , K	a	b	c	d	e	T_2 , K
1	493	45	75	5	25	75	463
2	753	30	75	5	25	75	703
3	873	40	80	10	40	80	733
4	923	40	75	10	40	86	768
5	1173	55	90	10	40	72	1123
6	1173	40	85	10	40	95	973
7	723	55	75	10	40	70.5	503
8	1173	35	90	10	50	75	1093
9	1073	35	85	5	35	85	923
10	1023	25	75	5	25	85	923
11	773	55	80	10	25	60	533
12	773	42	80	10	40	90	643
13	973	60	90	10	50	75	833
14	1033	45	95	10	45	75	983
15	673	30	50	5	30	50	543
16	1273	15	—	5	20	40	1113
17	773	40	75	10	40	80	603
18	873	50	80	10	50	90	753
19	523	40	75	10	40	95	443
20	923	50	80	10	50	85	703
21	873	40	90	10	40	75	793
22	873	30	95	10	30	60	733
23	1273	50	90	10	50	85	1073
24	723	50	85	10	20	75	673
25	723	35	60	10	50	60	583

phases; (3) determine the composition of the stable chemical compound; (4) determine the qualitative and quantitative compositions of the eutectic mixtures; (5) plot all types of cooling curves possible for a given system and indicate the states on the fusion diagram to which these curves correspond; (6) determine the phase states of systems containing c , d , and $e\%$ A at temperature T_1 and find out what will happen to these systems if they are cooled to temperature T_2 ; (7) determine the number of phases and that of conditional thermodynamic degrees of freedom of the system at the eutectic point and with 95 and 5% mol. A; (8) determine the temperature at which a melt with $c\%$ A will start solidifying, the temperature at which the melt will solidify completely, and the composition of the first crystals; (9) determine the temperature at which a system with $d\%$ A will start melting, the temperature at which it will melt completely, and the composition of the first drops of the melt; (10) calculate the heats of fusion of substances A and B; and (11) determine which component and in what amount will crystallize from the system if 2 kg of a melt with $a\%$ A are cooled from T_1 to T_2 .

CHAPTER 16

Heterogeneous Equilibrium in Ternary Systems Containing Liquid and Solid Phases

Basic Equations and Symbols

A point on the plane of an equilateral triangle represents the composition of a ternary system. If perpendiculars are dropped from point P (Fig. 36a) to the sides of the triangle, the sum of these perpendicular lines equals the height of the triangle, which is taken as 100% (Gibbs' triangle). And if lines parallel with the sides of the triangle are drawn from point P (Fig. 36b), their sum equals the triangle side which is taken as 100% (Roozeboom's triangle). The apices of the triangle correspond to the pure components (characteristic points).

Binary systems are represented on respective sides of an equilateral triangle. Lines parallel to the sides of the triangle represent the *locus of points corresponding to systems with a constant content of the component associated with a particular side*. The straight lines drawn from the apices of the triangle to the points of intersection with the opposite sides represent the *locus of points corresponding to the systems in which the ratio of two components remains constant and equal to that of the portions into which the associated side of the triangle is divided* (characteristic lines).

Let the overall composition of a binary system be represented by point P (Fig. 36a), the composition of the first phase (I) be represented by point M , and that of the second phase (II) be represented by point N . Then, if the composition is given in terms of weight percentage,

$$m_I/m_{II} = NP/PM \quad (16.1)$$

where m_I and m_{II} stand for the weights of the first and the second

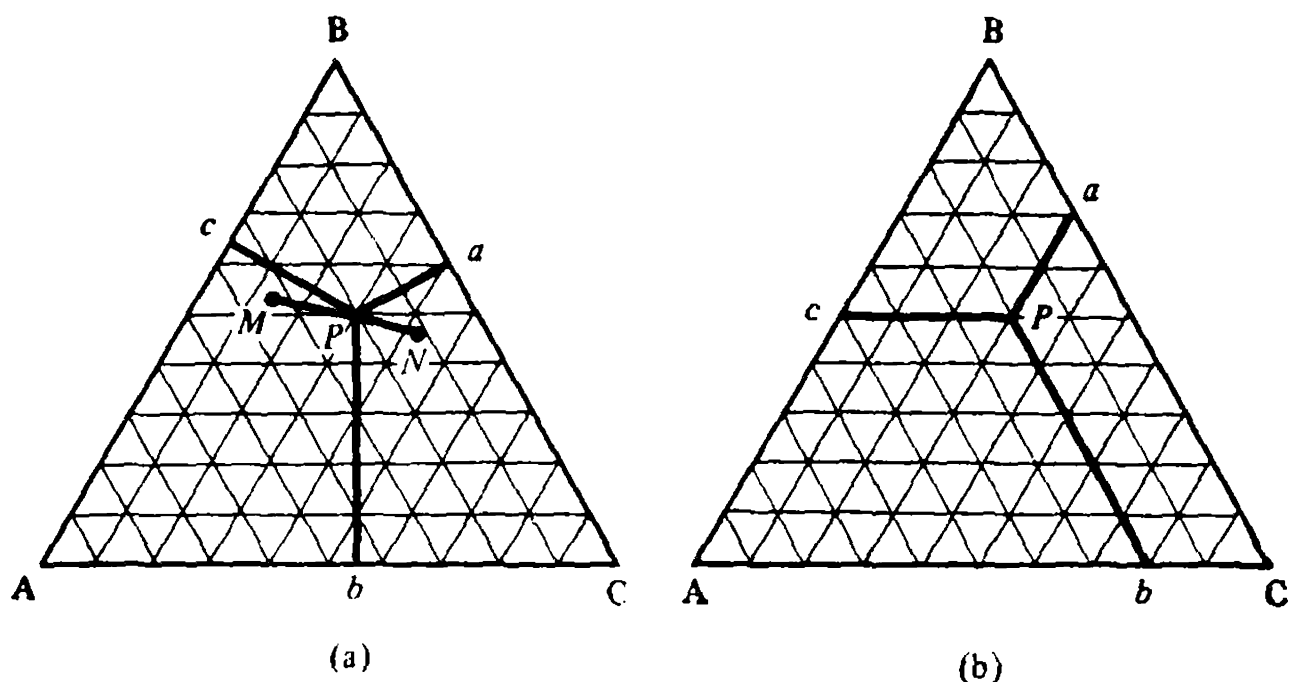


Fig. 36. Presentations of ternary system compositions by Gibbs' (a) and Roozeboom's (b) methods

phase, respectively. If the composition is expressed as mole percentage, then

$$n_I/n_{II} = NP/PM \quad (16.2)$$

where n_I and n_{II} stand for the number of moles in the first and the second phase, respectively.

Exercises

1. Analyse the phase state of a nonisomorphic ternary system ABC (Fig. 37). Analyse the process of cooling of the system whose composition is represented in the diagram by point 1.

Solution. Above surfaces $adgf$, $bdge$, and $cfge$ all systems are homogeneous, in the form of liquid melts. Surface $adgf$ represents the composition of the melt which is at equilibrium with the crystals of component A. Surface $bdge$ represents the composition of the melt at equilibrium with the crystals of component B. And surface $cfge$ represents the composition of the melt at equilibrium with the crystals of component C. Lines dg , fg , and eg of intersection of the above sur-

faces represent the compositions of the melts at equilibrium with the crystals of two components, line dg corresponding to equilibrium with the crystals of A and B, line eg corresponding to equilibrium with the crystals of B and C, and line fg corresponding to equilibrium with the crystals of A and C. Corresponding to point g of intersection of lines dg , eg , and fd is the equilibrium between the melt and the crystals of all three components A, B, and C. Points d , e , and f correspond to the binary eutectics. Below point g , which corresponds to the ternary eutectic mixture, all systems are heterogeneous, being represented by three solid phases.

We now follow the changes in the phase state of the system as it is being cooled. When the system has cooled down to temperature T_1 , it is homogeneous, being represented by a single liquid phase. At T_1 , crystallization of component A begins (point 2). Since only component A passes from the melt into the solid phase, the concentration ratio of components B and C in the liquid melt remains the same. On the plane triangle of the prism's base this process is represented by line $1'-3'$. The composition of the melt changes along line $2-3$. At

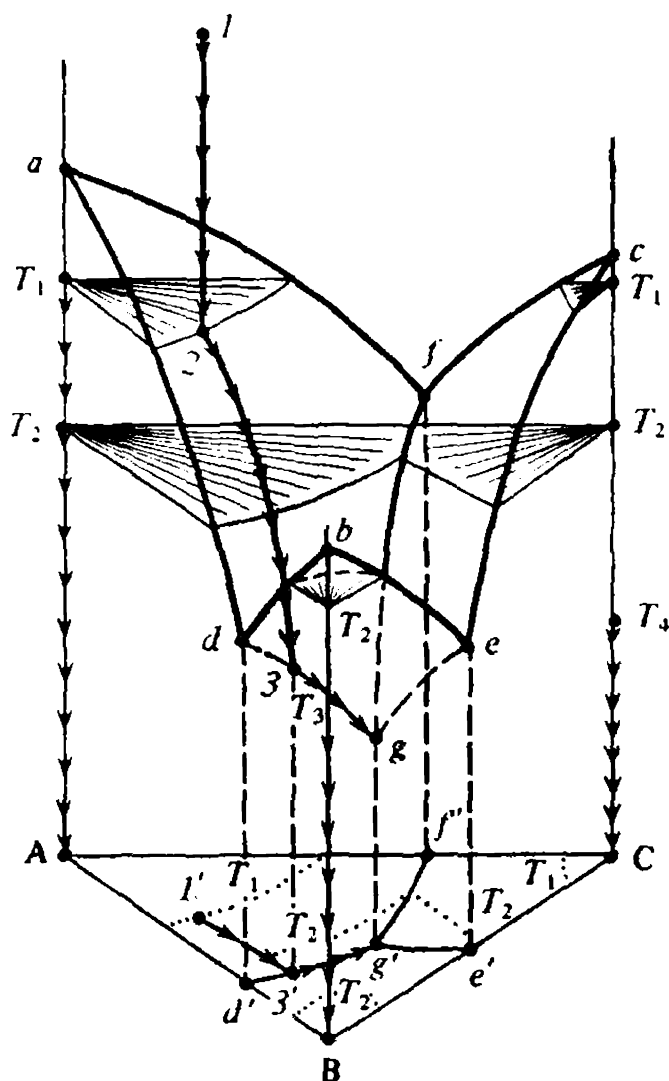


Fig. 37. Melting-point diagram for a nonisomorphic ternary system

point 3, the melt becomes saturated not only with component A but also with component B. Point 3 corresponds to temperature T_3 . At this temperature, component B starts crystallizing from the melt along with component A. The composition of the melt changes along line $3-g$. On the plane triangle, this process is represented by line $3'-g'$. The ternary eutectic mixture (point g) has temperature T_4 at which the entire system crystallizes and becomes a heterogeneous three-phase one. As the temperature of the system continues going down, the crystals of components A, B, and C become cooled, which is represented on the diagram by the arrows on the prism edges. All of the cooling process is represented by arrows in Fig. 37.

2. Determine the amount of component A passing into the solid

phase from 1 kg of a system cooled down to temperature T_2 . The composition of the system is represented by point 1 (Fig. 37). The projection of the T_2 isotherm on the prism base divides portion $1'-3'$ into two parts at a ratio of 13 : 4. The composition is given as weight percentage.

Solution. To determine the weight ratio between the liquid and solid phases use the lever principle:

$$m_s / (1 - m_s) = 4/13 = 0.308, \quad m_s = 0.308 - 0.308m_s$$

$$m_s = 0.235 \text{ kg}$$

Since only component A passes from the system whose composition is represented by point 1 into the solid phase, the weight of its crystal at temperature T_2 will be 0.235 kg. The weight of the remaining melt will be 0.765 kg.

3. The NaCl-KCl-H₂O system is nonisomorphous. No chemical compounds are formed between the components. The initial system contains 10 kg KCl, 20 kg NaCl, and 70 kg H₂O. The water solubilities of the components at 373 K are 56.2 kg KCl and 39.4 kg NaCl per 100 kg of solution. The combined solubility is 27.39 kg NaCl and 35.16 kg KCl in 100 kg of solution.

(1) Draw the phase diagram of the system, assuming that the solubility lines are straight. (2) Determine

the amount of evaporated water and the composition of the solution before crystallization begins. (3) Which salt, NaCl or KCl, will start crystallizing from solution during isothermal evaporation of water from the initial system? (4) How much water will evaporate before crystallization of the two salts? (5) How many kilograms of NaCl and KCl will pass into the solid phase if 95% of the water present in the initial system will be evaporated from it?

Solution. Given the compositions of the initial system, the binary eutectic mixtures NaCl-H₂O and KCl-H₂O, and the ternary eutectic mixture NaCl-KCl-H₂O, mark, respectively, points p_1 , e_1 , e_2 , and e_3 on the triangular diagram. Connect points e_1 and e_3 , e_2 and e_3 by straight lines (Fig. 38). Since only water evaporates from the solution whose composition is represented by point p_1 on the phase diagram, the ratio between NaCl and KCl in the system remains unchanged. The evaporation process is represented by extension of the line connecting point p_1 with the H₂O apex of the triangle, that is by

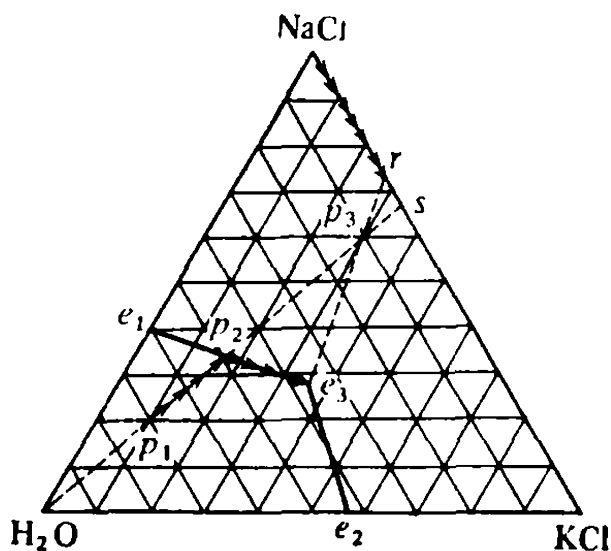


Fig. 38. Isothermal section of the phase diagram for a NaCl-KCl-H₂O system

line p_1-p_2 . At point p_2 , the solution becomes saturated with NaCl, and the latter begins to crystallize. Calculate the amount of water to be evaporated in the process represented by line p_1-p_2 on the diagram. Determine the composition at p_1 : 16.5% KCl, 33.5% NaCl, and 50% H_2O . Calculate the weight of water in the system corresponding to point p_2 : for the composition at p_2 (10 + 20) kg of the salts constitute 50%, whereas x kg of water account for the other 50%. Hence, $x = 30$ kg. Thus, after evaporation of water, 10 kg KCl, 20 kg NaCl, and 30 kg H_2O will remain in the system whose composition is represented by point p_2 . 40 kg of water have been evaporated from the system before NaCl started to crystallize. Since NaCl will pass from the system into the solid phase during evaporation of water, the system will become richer in KCl. This process is represented by line p_2-e_3 . At point e_3 , NaCl will start crystallizing together with KCl. Determine the amount of water to be evaporated before both salts start crystallizing. Since only NaCl crystallizes from the solution (line p_2-e_3), all of KCl will remain in the solution. At point e_3 the weight percentage of the components will be as follows: 27.39% NaCl, 35.16% KCl, and 37.45% H_2O .

10 kg KCl in the solution of composition e_3 —	35.16%
x kg H_2O in the same solution	—37.45%

Consequently, $x = 10.65$ kg H_2O will remain in the solution. The amount of water evaporation is $70 - 10.65 = 59.35$ kg.

In order to determine the amounts of NaCl and KCl crystallizing from the system during evaporation of 95% H_2O , calculate the composition of the resulting system. The overall composition will be 10 kg KCl, 20 kg NaCl, and $70 \times 0.05 = 3.50$ kg H_2O , the weight percentages being 29.85% KCl, 59.70% NaCl, and 10.45% H_2O . Corresponding to this composition will be point p_3 on the diagram. Connect points e_3 and p_3 and extend the line connecting these points till it intersects the NaCl-KCl base of the triangle. The intersection will be at point r . The amount of the salts passing into the solid phase relates to that of the entire system as the length of portion p_3e_3 relates to that of portion re_3 , which corresponds to 0.702. The total weight of the system is 33.5 kg. The weight of the solid phase is $33.5 \times 0.702 = 23.52$ kg, and that of the remaining solution is $33.5 - 23.52 = 9.98$ kg.

The composition of the solid phase will be represented by point r on the diagram, which corresponds to 73% NaCl and 27% KCl. The solid phase will contain 17.17 kg NaCl and 6.35 kg KCl. The solution is essentially a ternary eutectic mixture. Its weight is 9.98 kg, and it contains 2.80 kg NaCl, 3.68 kg KCl, and 3.50 kg H_2O . When all of the water present in the initial solution evaporates, the composition of the system will be represented in the diagram by point s .

Problems

1. A system contains salts S_I and S_{II} having common ions, as well as water. The composition of the system is 20% S_I , 25% S_{II} , and 55% H_2O . The eutectic mixtures S_I H_2O and S_{II} H_2O contain 60% and 50% S , respectively. The composition of the ternary eutectic mixture is 50% S_I , 25% S_{II} , and 25% H_2O . Draw the isothermal section of the phase diagram at a temperature above that of crystallization of water but below that of crystallization of the binary eutectic mixture salt-salt. Follow the process of isothermal evaporation of water from the system.

2. Follow, on the phase diagram of a system containing two salts S_I and S_{II} with common ions plus water, the isothermal evaporation of water from a solution containing 15% S_I , 25% S_{II} , and 60% H_2O . The solubility of salt S_I in water is 45%, and that of salt S_{II} is 50%. The combined solubility of salts S_I and S_{II} is 40 and 25%, respectively. Assuming that the solubility lines are straight, determine which salt will be the first to start crystallizing during isothermal evaporation of water, how much water is to be evaporated from 1 kg of the above system before the first crystal starts forming, and how much water is to be evaporated before the onset of cocrystallization of salts S_I and S_{II} .

3. Proceeding from the isothermal section of the phase diagram of a Tl_2Cl_2 - $Tl_2(NO_3)_2$ - Tl_2SO_4 system, given in the handbook, determine the amount of Tl_2SO_4 which will crystallize from a system containing 20% Tl_2Cl_2 , 20% $Tl_2(NO_3)_2$, and 60% Tl_2SO_4 , when the system is cooled down to 400 °C.

Multivariant Problem

A ternary system H_2O -A-B contains salts A and B which do not form chemical compounds with each other and with water.

(1) Given the contents of the salt-water eutectics and the ternary eutectic, draw the isothermal section of the system at a temperature above the melting point of ice but below that of the eutectic salt-water.

(2) Mark point p corresponding to the composition of the initial system on the diagram.

(3) Which salt and in which amount will crystallize from 1 kg of the system during isothermal evaporation of water?

(4) Determine the amounts of salts A and B which will pass into the solid phase after evaporation of 90% of the water present in the initial system.

(5) Calculate the ratio between salts A and B in the solid phase after evaporation of 90% of water from the system.

Variant	Weight percentage in the system at point <i>p</i>		Weight percentage in the eutectics		Weight percentage in the ternary eutectic		
	A	B	A	B	A	B	H ₂ O
1	30	10	70	50	40	30	30
2	20	10	80	60	40	30	30
3	10	10	60	80	30	30	40
4	20	30	50	70	20	50	30
5	20	20	70	50	20	30	50
6	20	10	40	50	40	30	30
7	10	30	60	80	30	30	40
8	10	20	50	70	30	40	30
9	10	40	70	50	30	30	40
10	30	10	80	60	30	40	30
11	20	10	60	80	50	30	20
12	10	10	50	70	40	30	30
13	20	30	70	50	40	30	30
14	20	20	80	60	30	40	30
15	20	10	60	80	40	30	30
16	10	30	50	70	40	20	40
17	10	20	70	50	40	40	20
18	10	40	80	60	40	40	20
19	30	10	60	80	30	40	30
20	20	10	50	70	40	40	20
21	10	10	70	50	50	30	20
22	20	30	80	60	50	30	20
23	20	20	60	80	30	30	40
24	30	10	50	70	50	20	30
25	10	20	70	50	50	20	30

CHAPTER 17
Chemical Equilibrium

Basic Equations and Symbols

The mass action law for a reaction having the following general form:



and proceeding in the gas phase under conditions where the laws of ideal gaseous state apply is given by the equation

$$K_c = c_D^{\nu_D} c_E^{\nu_E} / c_A^{\nu_A} c_B^{\nu_B} \tag{17.1}$$

where c_i is the equilibrium molar concentration of the i th component;

$$c_i = P_i/RT \quad (17.2)$$

where P_i is the equilibrium partial pressure of the i th component;

$$K_P = P_D^{\nu_D} P_E^{\nu_E} / P_A^{\nu_A} P_B^{\nu_B} \quad (17.3)$$

$$P_i = x_i P \quad (17.4)$$

$$K_P = \frac{x_D^{\nu_D} x_E^{\nu_E}}{x_A^{\nu_A} x_B^{\nu_B}} P^{\nu_D + \nu_E - \nu_A - \nu_B} = \frac{x_D^{\nu_D} x_E^{\nu_E}}{x_A^{\nu_A} x_B^{\nu_B}} P^{\Delta \nu} \quad (17.5)$$

where x_i is the equilibrium molar fraction of the i th component, P is the total pressure of the equilibrium mixture, and $\Delta \nu$ is the change in the number of moles of the substances in the ideal gaseous state;

$$\Delta \nu = \sum_i (\nu_i)_f - \sum_i (\nu_i)_i \quad (17.6)$$

where ν_i is the stoichiometric coefficient of the reaction;

$$x_i = \frac{n_i}{\sum_i n_i} = \frac{n_i}{n_A + n_B + n_E + n_D + n_{in}} \quad (17.7)$$

where n_i is the number of moles of the i th component in the equilibrium mixture, n_{in} is the number of moles of the inert gas (gas that does not participate in the chemical reaction), and $x_D \times 100$, $x_E \times 100$ is the equilibrium percentage yield of the reaction products.

The relationship between the equilibrium constant expressed in terms of partial pressures and that expressed in terms of concentrations is

$$K_P = K_c (RT)^{\Delta \nu} \quad (17.8)$$

The equilibrium constant can also be expressed in terms of the degree of conversion (α). Here the exact form of the equation $K_P = f(\alpha, P)$ depends on the reaction type. For example, for the reaction



$$K_P = [\alpha^2 (3 - \alpha)] / [(1 - \alpha)^3 P] \quad (17.9)$$

$$\alpha_A = \Delta n_A / n_A^0, \quad \alpha_B = \Delta n_B / n_B^0 \quad (17.10)$$

where α_A and α_B stand for the fractions of the initial substances that have undergone the chemical transformation (degree of transformation), while Δn_A and Δn_B stand for the number of moles of components A and B that have undergone the transformation;

$$\Delta n_A = n_A^0 - n_A, \quad \Delta n_B = n_B^0 - n_B \quad (17.11)$$

where n_A^0 and n_B^0 are the number of moles of substances A and B in the initial state of the system, n_A and n_B stand for the number of moles of substances A and B in the equilibrium state of the system. If substances A and B are taken in a stoichiometric ratio, then

$$n_B^0 = 2n_A^0 \quad (17.12)$$

and

$$\alpha_B = 2 (\Delta n_A) / 2n_A^0 = \alpha_A \quad (17.13)$$

The measure (depth) ξ of the reaction is

$$\xi = \Delta n_i / \nu_i \quad (17.14)$$

For reaction (a),

$$\xi = \Delta n_A / 1 = \Delta n_B / 2 \quad (17.15)$$

For relation (17.14) Eq. (17.15) takes the form

$$\xi = \alpha \quad (17.16)$$

The van't Hoff equation for the isotherm of reaction (a) is

$$\Delta G_{P,T} = RT \ln \frac{P_D^{\nu_D} P_E^{\nu_E}}{P_A^{\nu_A} P_B^{\nu_B}} - RT \ln K_P \quad (17.17)$$

$$\Delta A_{V,T} = RT \ln \frac{c_D^{\nu_D} c_E^{\nu_E}}{c_A^{\nu_A} c_B^{\nu_B}} - RT \ln K_c \quad (17.18)$$

where P_A , P_B , P_D , and P_E are the partial pressures of the initial substances and reaction products, and c_A , c_B , c_D , and c_E are the molar concentrations of the initial substances and reaction products;

$$\Delta A_{V,T} = \Delta G_{P,T} \quad (17.19)$$

For the standard state of the system,

$$\Delta G^\circ = -RT \ln K_P \quad (17.20)$$

$$\Delta A^\circ = -RT \ln K_c \quad (17.21)$$

$$\Delta A^\circ \neq \Delta G^\circ \quad (17.22)$$

In the SI system, Eq. (17.20) takes the form

$$\Delta G_{T(SI)}^\circ = \Delta G_{T(atm)}^\circ + \Delta \nu RT \ln 1.0133 \times 10^5 \quad (17.23)$$

where the subscripts (SI) and (atm) indicate that the equilibrium pressures are given in pascals and atmospheres, respectively.

Calculation of Gibbs' energy ΔG_{298}° for reactions in the standard state and 298 K is based on the equation

$$\Delta G_{298}^\circ = \Delta H_{298}^\circ - 298 \Delta S_{298}^\circ \quad (17.24)$$

where ΔH_{298}° is the heat of the reaction at 298 K, and ΔS_{298}° is the change in entropy of the reaction at standard pressure and 298 K.

Calculation of Gibbs' energy ΔG_T° for the reaction by the quantum-statistical method is based on the equation

$$\frac{\Delta G_T^\circ}{T} = \Delta \left(\frac{G^\circ - H_0^\circ}{T} \right) + \frac{\Delta H_0^\circ}{T} \quad (17.25)$$

where $\frac{(G^\circ - H_0^\circ)}{T}$ is the reduced Gibbs energy, and ΔH_0° is the hypothetical heat of the reaction at absolute zero in the ideal gaseous state;

$$\Delta H_0^\circ = \Delta H_T^\circ - \Delta (H_T^\circ - H_0^\circ) \quad (17.26)$$

The values of $(H_T^\circ - H_0^\circ)$ are calculated by the quantum-statistical method.

Calculation of Gibbs' energy ΔG_T° for the reaction by the thermodynamic (Temkin-Shvartsman) method is based on the equation

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \int_{298}^T \Delta C_P dT - T \int_{298}^T \frac{\Delta C_P}{T} dT \quad (17.27)$$

Substitution of the temperature dependence of ΔC_P° :

$$\Delta C_P^\circ = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3 + \frac{\Delta c'}{T^2} \quad (17.28)$$

into Eq. (17.27) gives

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ - T(M_0\Delta a + M_1\Delta b + M_2\Delta c + M_3\Delta d + M_{-2}\Delta c') \quad (17.29)$$

The coefficients M_0 , M_1 , M_2 , M_3 , and M_{-2} have been calculated and are given in handbooks for several temperatures.

The temperature dependence of the equilibrium constant of a reaction is given by the van't Hoff isobar (isochore) equation in the following differential form:

$$\frac{d \ln K_P}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (17.30)$$

$$\frac{d \ln K_c}{dT} = \frac{\Delta U^\circ}{RT^2} \quad (17.31)$$

Equations (17.30) and (17.31) can be integrated for the following conditions:

$$(1) \Delta H^\circ = \text{const}, \quad \Delta C_P^\circ = 0, \quad \log K_P = -\frac{\Delta H^\circ}{2.3026RT} + \text{const} \quad (17.32)$$

$$(2) \Delta H^\circ \neq \text{const}, \quad \Delta C_P^\circ = \text{const}, \quad \Delta C_P^\circ = \Delta a,$$

$$\log K_P = -\frac{A}{T} + B \log T + C \quad (17.33)$$

or

$$\log K_P = \frac{\Delta H_{298}^\circ - \Delta a 298}{2.3026RT} + \frac{\Delta a}{R} \log T + \text{const} \quad (17.34)$$

$$(3) \Delta H^\circ \neq \text{const}, \quad \Delta C_P^\circ = \Delta a + \Delta b T$$

$$\log K_P = \frac{A}{T} + B \log T + DT + C \quad (17.35)$$

or

$$\log K_P = \frac{\Delta a 298 + \frac{\Delta b}{2} 298^2}{2.3026RT} + \frac{\Delta a}{R} \log T + \frac{\Delta b}{2 \times 2.3026R} T + \text{const} \quad (17.36)$$

$$(4) \Delta H^\circ \neq \text{const}, \quad \Delta C_P^\circ = \Delta a + \Delta b T + \Delta c T^2 + \frac{\Delta c'}{T^2}$$

$$\log K_P = \frac{A}{T^2} + \frac{B}{T} + C + D \log T + ET + FT^2 \quad (17.37)$$

The equilibrium in the gas phase at medium pressures is calculated as follows.

The equilibrium constant for reaction (a) will be

$$K_f = f_D^{\nu_D} f_E^{\nu_E} / f_A^{\nu_A} f_B^{\nu_B} = K_x K_\gamma P^{\Delta \nu} \quad (17.38)$$

where

$$K_x = x_D^{\nu_D} x_E^{\nu_E} / x_A^{\nu_A} x_B^{\nu_B} \quad (17.39)$$

$$K_\gamma = \gamma_D^{\nu_D} \gamma_E^{\nu_E} / \gamma_A^{\nu_A} \gamma_B^{\nu_B} \quad (17.40)$$

$$\gamma_i = f_i P \quad (17.41)$$

f_i being the fugacity of the i th component in the equilibrium mixture. It can be assumed without any significant error that

$$f_i = f_i^0 x_i \quad (17.42)$$

where f_i^0 is the fugacity of the pure i th component at the equilibrium mixture pressure, or

$$f_i = P \gamma_i x_i \quad (17.43)$$

the activity coefficient γ_i being determined by the corresponding states method.

Exercises

1. Calculate the degrees of transformation α , of the initial substances of the reaction $A + 4B = D$, the depth ξ of the reaction, and the equilibrium yield of the reaction product D ($x_D \times 100$) if the initial amounts of substances A and B are $n_A^0 = 1.000$ mole and

$n_B^0 = 12.000$ moles. Once equilibrium is reached, $n_A = 0.025$ mole, $n_B = 8.100$ moles, and $n_D = 0.975$ mole.

Solution. According to Eq. (17.10), the degrees of transformation will be

$$\alpha_A = \frac{1.000 - 0.025}{1} = 0.975 \quad \text{and} \quad \alpha_B = \frac{12.000 - 8.100}{12} = 0.325$$

To calculate the depth of the reaction use Eq. (17.14):

$$\xi = \frac{n_A^0 - n_A}{1} = \frac{n_B^0 - n_B}{4} = \frac{1.000 - 0.025}{1} = \frac{12.000 - 8.100}{4} = 0.975$$

Determine the equilibrium yield of substance D from the molar fraction of this substance while the system is in the state of equilibrium:

$$x_D = \frac{n_D}{n_A + n_B + n_D} = \frac{0.975}{0.025 + 8.100 + 0.975} = 0.107$$

The equilibrium yield of substance D will be $0.107 \times 100 = 10.7\%$.

2. Calculate the equilibrium constant K_c of the reaction $A + 4B = D$ if the volume of the reaction vessel is $V = 0.05 \text{ m}^3$.

Solution. According to Eq. (17.1),

$$K_c = \frac{c_D}{c_A c_B^4} = \frac{n_D/V}{n_A/V (n_B/V)^4} = \frac{0.975 \times 50^4}{0.025 \times 8.100^4} = 5.66 \times 10^4$$

3. The equilibrium constant of the reaction $H_2 + I_2 = 2HI$ at 693 K is $K_c = 50.25$. Calculate the yield of hydrogen iodide if $0.846 \times 10^{-3} \text{ kg } I_2$ and $0.0212 \times 10^{-3} \text{ kg } H_2$ have been placed in a vessel having a capacity of 10^{-3} m^3 .

Solution. Determine the number of moles of the initial substances:

$$n_{H_2}^0 = \frac{0.0212 \times 10^{-3}}{2} 10^3 = 0.0106 \text{ mole } H_2$$

$$n_{I_2}^0 = \frac{0.846 \times 10^{-3}}{254} 10^3 = 0.00333 \text{ mole } I_2$$

H_2	+	I_2	=	$2HI$	
10.6×10^{-3}		3.33×10^{-3}		0	numbers of moles in the initial state of the system
$10.6 \times 10^{-3} - x$		$3.33 \times 10^{-3} - x$		x	numbers of moles in the equilibrium state of the system

$$x = n_i^0 - n_i$$

Find K_c with the aid of Eq. (17.1):

$$K_c = \frac{(n_{\text{HI}}/V)^2}{(n_{\text{H}_2}/V)(n_{\text{I}_2}/V)} = \frac{4x^2/(10^{-3})^2}{[(10.6 \times 10^{-3} - x)/10^{-3}][(3.33 \times 10^{-3} - x)/10^{-3}]} = 50.25$$

Solution of this equation gives

$$46.25x^2 - 0.7015x + 1.7737 \times 10^{-3} = 0$$

$$\begin{aligned} \text{Hence } x_{1,2} &= \frac{0.7015 \pm \sqrt{0.7015^2 - 4 \times 1.7737 \times 10^{-3} \times 46.25}}{2 \times 46.25} \\ &= \frac{0.7015 \pm 0.4049}{92.50}, x_1 = 11.961 \times 10^{-3} \text{ and } x_2 = 3.206 \times 10^{-3} \end{aligned}$$

The first root, x_1 , makes no physical sense because x cannot exceed $n_{\text{H}_2}^0$ in magnitude; $x_2 = 3.206 \times 10^{-3}$ mole. The amount of HI resulting from establishment of the state of equilibrium will be $m_{\text{HI}} = 2xM_{\text{HI}} = 2 \times 3.206 \times 10^{-3} \times 128 \times 10^{-3} = 0.821 \times 10^{-3}$ kg.

4. A closed vessel having a capacity of 0.05 m^3 contains one mole of substance A and 12 moles of substance B. The reaction $\text{A} + 4\text{B} = \text{D}$ results in equilibrium. The total pressure in the equilibrium state of the system is $4.51 \times 10^5 \text{ Pa}$. Calculate the equilibrium concentrations of all reactants at 298 K . The system obeys the laws of ideal gaseous state.

Solution. According to the equation of the reaction, write the numbers of moles in the initial and equilibrium states:

A	+ 4B	= D	
1	12	0	numbers of moles in the initial state
$1 - x$	$12 - 4x$	x	numbers of moles in the equilibrium state

$$\sum n_i = 1 - x + 12 - 4x + x = 13 - 4x$$

According to the Clapeyron-Mendeleev equation ($PV = \sum_i n_i RT$),

$$\sum_i n_i = 13 - 4x = \frac{4.51 \times 10^5 \times 0.05}{8.3143 \times 298} = 9.10 \text{ moles}$$

$$x = \frac{13 - 9.10}{4} = 0.975 \text{ mole}$$

To determine the equilibrium concentrations, use the equation $c_i = n_i/V$:

$$c_A = \frac{1 - 0.975}{0.05} = 0.5 \text{ mole/m}^3$$

$$c_B = \frac{12 - 4 \times 0.975}{0.05} = 162 \text{ moles/m}^3$$

$$c_D = \frac{0.975}{0.05} = 19.5 \text{ moles/m}^3$$

5. At 693 K, hydrogen and iodine are confined in a closed vessel. In the initial state of the system, the partial pressures are $P_{\text{H}_2} = 0.4521 \times 10^5 \text{ Pa}$ and $P_{\text{I}_2} = 0.1682 \times 10^5 \text{ Pa}$. The equilibrium partial pressure of HI is $P_{\text{HI}} = 0.3222 \times 10^5 \text{ Pa}$. Calculate the equilibrium partial pressures of H_2 and I_2 and the equilibrium constant.

Solution. The decreases in the partial pressures of hydrogen and iodine (ΔP_{H_2} and ΔP_{I_2}) are equal:

$$P'_{\text{H}_2} = P_{\text{H}_2} - \Delta P_{\text{H}_2} \text{ and } P'_{\text{I}_2} = P_{\text{I}_2} - \Delta P_{\text{I}_2}$$

where P'_{H_2} and P'_{I_2} are the equilibrium partial pressures of hydrogen and iodine. The partial pressure of the resulting HI equals twice the decrease in the partial pressure of hydrogen:

$$P'_{\text{HI}} = 2\Delta P_{\text{H}_2} = 2\Delta P_{\text{I}_2}, \quad \Delta P = 0.3222 \times 10^5 / 2 = 0.1611 \times 10^5 \text{ Pa}$$

Then,

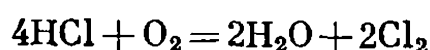
$$P'_{\text{H}_2} = 0.4521 \times 10^5 - 0.1611 \times 10^5 = 0.2910 \times 10^5 \text{ Pa}$$

$$P'_{\text{I}_2} = 0.1682 \times 10^5 - 0.1611 \times 10^5 = 0.0071 \times 10^5 \text{ Pa}$$

Calculate K_P using Eq. (17.3):

$$K_P = \frac{(P'_{\text{HI}})^2}{P'_{\text{H}_2} P'_{\text{I}_2}} = \frac{(0.3222 \times 10^5)^2}{0.2910 \times 10^5 \times 0.0071 \times 10^5} = 50.25$$

6. The process of chlorine production through oxidation of hydrogen chloride is based on the reaction



Mixing one mole of HCl with 0.480 mole of O_2 yields 0.402 mole of Cl_2 . Calculate K_P if the system is at $P = 1.0133 \times 10^5 \text{ Pa}$ and 659 K.

Solution. Formation of 0.402 mole Cl_2 requires 0.804 mole HCl and 0.201 mole O_2 . In the state of equilibrium,

$$n_{\text{Cl}_2} = n_{\text{H}_2\text{O}} = 0.402 \text{ mole}$$

$$n_{\text{HCl}} = 1.000 - 0.804 = 0.196 \text{ mole}$$

$$n_{\text{O}_2} = 0.480 - 0.201 = 0.279 \text{ mole}$$

$$\sum_i n_i = 0.196 + 0.279 + 0.402 + 0.402 = 1.279 \text{ moles}$$

Refer the equilibrium partial pressures to the standard one (1 atm):

$$P_{\text{H}_2\text{O}} = 0.402 / 1.279 = 0.314$$

$$P_{\text{Cl}_2} = 0.402 / 1.279 = 0.314$$

$$P_{\text{HCl}} = 0.196 / 1.279 = 0.153$$

$$P_{\text{O}_2} = 0.279 / 1.279 = 0.218$$

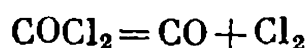
Then,

$$K_P = \frac{0.314^2 \times 0.314^2}{0.153^4 \times 0.218} = 81.376$$

7. At 823 K and 1.0133×10^5 Pa, the degree of dissociation of phosgene into carbon monoxide and chlorine is 77%. Determine K_P and K_c .

Solution. The dissociation process can be written as follows: $\text{COCl}_2 = \text{CO} + \text{Cl}_2$. The equilibrium partial pressure equals the total pressure times the equilibrium molar fraction:

$$P_{\text{CO}} = Px_{\text{CO}}, \quad P_{\text{Cl}_2} = Px_{\text{Cl}_2}, \quad \text{and} \quad P_{\text{COCl}_2} = Px_{\text{COCl}_2}$$



1 0 0 initial numbers of moles

1 - α α α equilibrium numbers of moles

$$\Sigma n_i = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

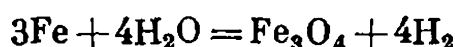
Hence, the equilibrium partial pressures referred to the standard one (1 atm) will be

$$P_{\text{CO}} = P_{\text{Cl}_2} = P \frac{\alpha}{1 + \alpha}, \quad P_{\text{COCl}_2} = P \frac{1 - \alpha}{1 + \alpha}$$

$$K_P = \frac{P^2 \alpha^2 (1 + \alpha)}{(1 + \alpha)^2 P (1 - \alpha)} = P \frac{\alpha^2}{1 - \alpha^2} = \frac{0.77^2}{1 - 0.77^2} = 1.456$$

$$K_c = K_P (RT)^{-\Delta v} = 1.456 (8.3143 \times 823)^{-1} = 21.56$$

8. In the reaction



at the initial water vapour pressure of 1.3325×10^5 Pa after equilibrium has been established at 473 K, the equilibrium partial pressure of the evolving hydrogen is 1.2717×10^5 Pa. Determine the yield of hydrogen if water steam is injected at 3.0399×10^5 Pa and 473 K into a $2 \times 10^{-3} \text{ m}^3$ vessel containing metallic iron.

Solution. Since the concentrations of metallic iron and Fe_3O_4 in the gas phase are virtually constant, the equilibrium constant of the reaction can be written as

$$K_P = P_{\text{H}_2}^4 / P_{\text{H}_2\text{O}}^4 \quad \text{or} \quad K'_P = P_{\text{H}_2} / P_{\text{H}_2\text{O}}$$

where $K'_P = K_P^{0.25}$. The reaction proceeds without any change in volume, therefore, when equilibrium is attained, $P_{\text{H}_2\text{O}} = 1.3325 \times 10^5 - 1.2717 \times 10^5 = 0.0608 \times 10^5 \text{ Pa} = 0.0600 \text{ atm}$.

$$P_{\text{H}_2\text{O}} = 1.2717 \times 10^5 \text{ Pa} = 1.2550 \text{ atm}, \quad K'_P = \frac{1.2550}{0.0600} = 20.917$$

To determine the molar yield of hydrogen use the Clapeyron-Mendeleev equation:

$$n_{\text{H}_2} = P_{\text{H}_2} V / RT$$

$$P_{\text{H}_2} = P_{\text{H}_2\text{O}} K'_P = (3.0399 \times 10^5 - P_{\text{H}_2}) K'_P$$

$$P_{\text{H}_2} = \frac{3.0399 \times 10^5 K'_P}{1 + K'_P} = \frac{3.0399 \times 10^5 \times 20.916}{21.916} = 2.9012 \times 10^5 \text{ Pa}$$

The hydrogen yield will be

$$G_{\text{H}_2} = 2n_{\text{H}_2} = 2 \frac{2.9012 \times 10^5 \times 2 \times 10^{-3}}{8.3143 \times 473} = 0.295 \text{ g} = 0.295 \times 10^{-3} \text{ kg}$$

9. Calculate the equilibrium yield of NO_2 in the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ at $1.0133 \times 10^5 \text{ Pa}$ and 298 K .

Solution. To determine the equilibrium yield one must know the equilibrium constant of the reaction. Take the necessary data from the handbook and calculate Gibbs' energy using the equation

$$\Delta G_{298}^\circ = \Delta H_{298}^\circ - 298 \Delta S_{298}^\circ$$

Substance	NO_2	N_2O_4
$\Delta H_f^\circ, 298^\circ, \text{ kJ/mole}$	33.89	9.37
$S_{298}^\circ, \text{ J mole}^{-1} \text{ K}^{-1}$	240.45	304.3
$\Delta H_{298}^\circ = 58.41 \text{ kJ}, \quad \Delta S_{298}^\circ = 176.6 \text{ J}$		
$\Delta G_{298}^\circ = 58.41 \times 10^3 - 298 \times 176.6 = 5.78 \times 10^3 \text{ J}$		

Use Eq. (17.20) to calculate K_P :

$$\log K_P = -\frac{5780}{2.3026 \times 8.3143 \times 298} = -1.0131 = \bar{2}.9869,$$

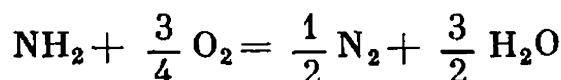
$$K_P = 0.0970$$

$$K_P = \frac{P x_{\text{NO}_2}^2}{1 - x_{\text{NO}_2}} = 0.0970, \quad x_{\text{NO}_2}^2 = 0.0970 - 0.0970 x_{\text{NO}_2}$$

$$x_{\text{NO}_2}^2 + 0.0970 x_{\text{NO}_2} - 0.0970 = 0$$

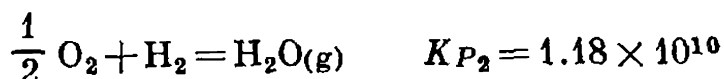
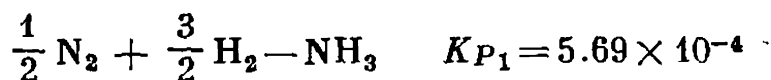
Solution of the second-degree equation gives two roots one of which makes no physical sense. Then, $x_{\text{NO}_2} = 0.2667$, and the equilibrium yield is $x_{\text{NO}_2} \times 100 = 26.67\%$.

10. Determine the equilibrium constant K_P of the reaction of ammonia oxidation:



at 1000 K . For the calculation use the following equilibrium constants of the reactions of ammonia and water formation from simple sub-

stances at 1000 K:



(pressure is given in atmospheres).

Solution. Derive an equation in which K_P to be found is related to the known values of K_{P_1} and K_{P_2} :

$$\Delta G^\circ = \frac{3}{2} \Delta G_{f, \text{H}_2\text{O}}^\circ - \Delta G_{f, \text{NH}_3}^\circ$$

where $\Delta G_{f,i}^\circ$ is the standard change in Gibbs' energy during formation of a given compound from simple substances, and ΔG° is the standard change in Gibbs' energy of the ammonia oxidation reaction.

$$-RT \ln K_P = -\frac{3}{2} RT \ln K_{P_2} + RT \ln K_{P_1}$$

or

$$K_P = \frac{K_{P_2}^3}{K_{P_1}} = \frac{(1.18 \times 10^{10})^3}{5.69 \times 10^{-4}} = 2.196 \times 10^{18}$$

11. The equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$ at 693 K is 50. Will the reaction yield hydrogen iodide, provided it is ideally reversible, if the initial concentrations are as follows (mole/litre): H_2 2, 1.5, 1; I_2 5, 0.25, 2; HI 10, 5, 10? The substances are fed into the reaction vessel from infinitely large containers. Hydrogen iodide is discharged from the reaction vessel into an infinitely large receptacle in which its concentration is c_{HI} .

Solution. Use the van't Hoff isotherm equation

$$\Delta G = \Delta A = RT \left(\ln \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} - \ln K_c \right)$$

to calculate ΔG or ΔA . Establish the sign of the result. To this end, calculate the values of $\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ and compare them with K_c :

(1) for the first arbitrary concentrations

$$\frac{10^2}{2 \times 5} = 10 < 50, \quad \Delta G < 0$$

the reaction will proceed spontaneously in the forward direction;

(2) for the second arbitrary concentrations

$$\frac{5^2}{1.5 \times 0.25} = 66.66 > 50, \quad \Delta G > 0$$

the reaction will not proceed spontaneously in the forward direction;

(3) for the third arbitrary concentrations

$$\frac{10^2}{2 \times 1} = 50 = 50, \Delta G = 0$$

the system is at equilibrium.

12. Express the equilibrium constant K_P of the reaction $\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O}_{(g)}$ in terms of total pressure P and degree of dissociation α of the water vapour.

Solution. If one proceeds from one mole of $\text{H}_2\text{O}_{(g)}$ ($n_{\text{H}_2\text{O}}^0 = 1$), then at the degree of dissociation α , $(1 - \alpha)$ mole H_2O ($n_{\text{H}_2\text{O}}$) will remain in the equilibrium mixture and $\alpha/2$ mole O_2 (n_{O_2}) will form. The total number of moles in the equilibrium mixture of the gases will be

$$\sum_i n_i = \alpha + \alpha/2 + 1 - \alpha = (\alpha + 2)/2$$

Then, the equilibrium partial pressures will be

$$\begin{aligned} P_{\text{H}_2} &= P \frac{\alpha}{(\alpha + 2)/2} = P \frac{2\alpha}{\alpha + 2} \\ P_{\text{O}_2} &= P \frac{\alpha/2}{(\alpha + 2)/2} = P \frac{\alpha}{\alpha + 2} \\ P_{\text{H}_2\text{O}} &= P \frac{1 - \alpha}{\frac{\alpha + 2}{2}} = P \frac{2(1 - \alpha)}{\alpha + 2} \end{aligned}$$

and the equilibrium constant of the reaction will be

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} = \frac{P 2(1 - \alpha) (\alpha + 2) (\alpha + 2)^{1/2}}{(\alpha + 2) P 2\alpha P^{1/2} \alpha^{1/2}} = \frac{(1 - \alpha) (\alpha + 2)^{1/2}}{P^{1/2} \alpha^{3/2}}$$

13. Determine the standard affinity^{*} of calcium oxide for carbon dioxide at 1.0133×10^5 Pa and 1130 K if the pressure of CaCO_3 dissociation at this temperature is 0.560×10^5 Pa.

Solution. Calculate the equilibrium constant of the reaction $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$, using the following relation:

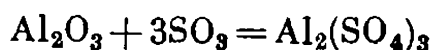
$$\Delta G_{1130}^\circ = -RT \ln K_P = -8.3143 \times 1130 \times 2.3026 \log K_P$$

Determine the equilibrium constant from the partial pressure of CO_2 (P_{CO_2}) in atmospheres because the pressure of 1 atm is considered to be the standard state.

$$K_P = \frac{1}{P_{\text{CO}_2}} = \frac{1}{0.560 \times 10^5} 1.0133 \times 10^5 = 1.8095$$

$$\Delta G_{1130}^\circ = -8.3143 \times 1130 \times 2.3026 \log 1.8095 = -5.5718 \times 10^3 \text{ J}$$

14. Determine the equilibrium constant of the reaction



at 298 K.

Solution. Calculate the heat of the reaction and the change in entropy at standard pressure and 298 K, using the necessary data from the handbook, namely, the heats of formation and absolute entropies:

Substance	$\text{Al}_2(\text{SO}_4)_3$	Al_2O_3	SO_3
$\Delta H_{f,298}^\circ$, kJ/mole	-3434	-1675	-395.2
S° , J mole ⁻¹ K ⁻¹	239.2	50.94	256.23

For the above reaction,

$$\Delta H_{298}^\circ = -573.4 \text{ kJ}, \quad \Delta S_{298}^\circ = -580.43 \text{ J/K}$$

Use Eq. (17.24) to determine the standard affinity:

$$\Delta G_{298}^\circ = -573.4 \times 10^3 - 298(-580.43) = -400.43 \times 10^3 \text{ J}$$

To determine the equilibrium constant use Eq. (17.20):

$$\log K_P = -\frac{\Delta G_{298}^\circ}{2.3026 R 298} = \frac{400.43 \times 10^3}{2.3026 \times 8.3143 \times 298} = 70.1885$$

15. Determine the equilibrium constant of the reaction $\text{SO}_2 + 0.5\text{O}_2 = \text{SO}_3$ at 700 K if $K_P = 588.9$ at 500 K (the pressure is expressed in Pa) and the heat of the reaction in the above temperature range is -99.48 kJ .

Solution. Use Eq. (17.32) at $\Delta H_T^\circ = \text{const}$:

$$\log K_{P, 500} = -\frac{\Delta H_T^\circ}{2.3026 \times 8.3143 \times 500} + B$$

$$\log K_{P, 700} = -\frac{\Delta H_T^\circ}{2.3026 \times 8.3143 \times 700} + B$$

$$\begin{aligned} \log K_{P, 700} &= \log K_{P, 500} - \frac{\Delta H_T^\circ}{2.3026 \times 8.3143} \left(\frac{1}{700} - \frac{1}{500} \right) \\ &= \log 588.9 + \frac{99.48 \times 10^3}{19.1445} \left(\frac{1}{700} - \frac{1}{500} \right) = -0.1996 \end{aligned}$$

$$K_{P, 700} = 0.632$$

16. Write the temperature dependence of $\log K_P$ for the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Define the temperature range in which this dependence will hold. Calculate K_P at 700 K.

Solution. Find the relation $\log K_P = f(T)$. To this end, write the temperature dependence of ΔG_P° . The solution is most convenient in tabular form:

Substance	$\Delta H_f^\circ, 298,$ kJ/mole	$S_{298}^\circ,$ J mole ⁻¹ K ⁻¹	$C_P^\circ = f(T), \text{ J mole}^{-1} \text{ K}^{-1}$			Temperature range, K
			a	$b \times 10^3$	$c' \times 10^{-5}$	
CO ₂	-393.51	213.6	44.14	9.04	-8.53	298-2500
H ₂	0	130.6	27.28	3.26	0.502	298-3000
CO	-110.5	197.4	28.41	4.10	-0.46	298-2500
H ₂ O(g)	-241.84	188.74	30.00	10.71	0.33	298-2500

For the reaction,

$$\Delta H_{298}^\circ = -41.17 \times 10^3 \text{ J}, \quad \Delta S_{298}^\circ = 41.94 \text{ J/K}$$

$$\Delta a = 13.01, \quad \Delta b = -2.51 \times 10^{-3}, \quad \Delta c' = -7.90 \times 10^5$$

The temperature range in which the calculated values hold is 298 to 2500 K. Calculate $\log K_P$ at 298 K using Eq. (17.20):

$$\log K_{P, 298} = -\frac{-41.17 \times 10^3 - 298 \times 41.94}{2.3026 \times 8.3143 \times 298} = 5.0257$$

Find the temperature dependence of the heat of the reaction using Kirchhoff's law (6.31):

$$\frac{d \Delta H^\circ}{dT} = \Delta C_P^\circ = 13.01 - 2.51 \times 10^{-3} T - \frac{7.90 \times 10^5}{T^2}$$

$$\begin{aligned} \Delta H_T^\circ &= \Delta H_{298}^\circ + 13.01 (T - 298) - \frac{2.51 \times 10^{-3}}{2} (T^2 - 298^2) \\ &\quad + 7.90 \times 10^5 \left(\frac{1}{T} - \frac{1}{298} \right) = -41.17 \times 10^3 - 13.01 \times 298 \\ &\quad + \frac{2.51 \times 10^{-3}}{2} 298^2 - \frac{7.90 \times 10^5}{298} + 13.01 T - 1.255 \times 10^{-3} T^2 \\ &\quad + \frac{7.90 \times 10^5}{T} \end{aligned}$$

$$\Delta H_T^\circ = -47.586 \times 10^3 + 13.01 T - 1.255 \times 10^{-3} T^2 + 7.90 \times 10^5 / T$$

Substitute the derived relation into van't Hoff's isobar equation (17.30) and integrate between 298 and T :

$$d \ln K_P = \frac{-47.586 \times 10^3 + 13.01 T - 1.255 \times 10^{-3} T^2 + \frac{7.90 \times 10^5}{T}}{RT^2} dT$$

$$\ln K_{P, T} = \ln K_{P, 298} + \int_{298}^T \left(-\frac{5.723 \times 10^3}{T^2} + \frac{1.565}{T} - 0.151 \times 10^{-3} \right) dT$$

$$\begin{aligned}
& + \frac{0.950 \times 10^5}{T^3} \Big) dT = 11.572 + 5.723 \times 10^3 \left(\frac{1}{T} - \frac{1}{298} \right) + 1.565 \ln T \\
& - 1.565 \ln 298 - 0.151 \times 10^{-3} (T - 298) - \frac{0.950 \times 10^5}{2} \left(\frac{1}{T^2} - \frac{1}{298^2} \right) \\
& = 11.572 - 19.205 - 8.916 + 0.045 + 0.535 + \frac{5.723}{T} \\
& \quad + 1.565 \ln T - 0.151 \times 10^{-3} T - \frac{0.475 \times 10^5}{T^2}
\end{aligned}$$

Finally, we derive an equation of the $\log K_P = f(T)$ type:

$$\ln K_{P,T} = -15.969 + \frac{5.723 \times 10^3}{T} + 1.565 \ln T - 0.151 \times 10^{-3} T - \frac{0.475 \times 10^5}{T^2}$$

or

$$\begin{aligned}
\log K_{P,T} = & -\frac{0.206 \times 10^5}{T^2} + \frac{2.485 \times 10^3}{T} \\
& - 6.935 + 1.565 \log T - 0.066 \times 10^{-3} T
\end{aligned}$$

This equation holds in the temperature range of 298 to 2500 K. To determine $\log K_P$ at any temperature in the range of 298 to 2500 K substitute the temperature into the equation:

$$\begin{aligned}
\log K_{P,700} = & -\frac{0.206 \times 10^5}{700^2} + \frac{2.485 \times 10^3}{700} - 6.935 + 1.565 \log 700 \\
& - 0.066 \times 10^{-3} \times 700 = -0.042 + 3.550 - 6.935 \\
& \quad + 4.453 - 0.046 = 0.980 \\
K_{P,700} = & 9.55
\end{aligned}$$

17. The temperature dependence of the equilibrium constant for the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ is given by the equation

$$\log K_a = \frac{9411.7}{T} - 1.312 \log T + 0.128 \times 10^{-3} T + \frac{0.11 \times 10^5}{T} + 4.9$$

Determine the heat of the reaction at 1000 K.

Solution. Transform \log into \ln :

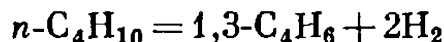
$$\ln K_a = \frac{21.671 \times 10^3}{T} - 1.312 \ln T + 0.295 \times 10^{-3} T + \frac{0.253 \times 10^5}{T^2} + 11.28$$

According to Eq. (17.26), $\Delta H_T^\circ = RT^2 \frac{d \ln K}{dt}$

$$\begin{aligned}
\Delta H_T^\circ = & RT^2 \left(-\frac{21.671 \times 10^3}{T^2} - \frac{1.312}{T} + 0.295 \times 10^{-3} - \frac{0.506 \times 10^5}{T^3} \right) \\
= & -180.179 \times 10^3 - 10.908 T + 2.453 \times 10^{-3} T^2 - \frac{4.207 \times 10^5}{T}
\end{aligned}$$

$$\begin{aligned}
\Delta H_{1000}^\circ = & -180.179 \times 10^3 - 10.908 \times 10^3 + 2.453 \times 10^3 \\
& - 0.421 \times 10^3 = -189.055 \times 10^3 \text{ J}
\end{aligned}$$

18. Determine the equilibrium constant of the reaction



at 800 K. Use the values of $\left(\frac{G^\circ_T - H^\circ_0}{T}\right)$ and ΔH°_0 , given in the handbook.

Solution. Calculate ΔG°_{800} using Eq. (17.25) and determine K_P from the standard affinity. Find the values of $\left(\frac{G^\circ_{800} - H^\circ_0}{T}\right)$ and ΔH°_0 in the handbook:

Substance	1,3-C ₄ H ₆	H ₂	n-C ₄ H ₁₀
$\left(\frac{G^\circ_{800} - H^\circ_0}{T}\right)$, J mole ⁻¹ K ⁻¹	-298.07	-130.482	-333.17
ΔH°_0 , kJ/mole	125.95	0	-97.981

For the above reaction,

$$\Delta \left(\frac{G^\circ_{800} - H^\circ_0}{T} \right) = -225.864 \text{ J/K}, \quad \Delta H^\circ_0 = 223.931 \text{ kJ}$$

$$\begin{aligned} \log K_{P(\text{atm})} &= -\frac{1}{2.3026R} \left[\Delta \left(\frac{G^\circ_{800} - H^\circ_0}{T} \right) + \frac{\Delta H^\circ_0}{T} \right] \\ &= -\frac{1}{19.1445} \left(-225.864 + \frac{223.931 \times 10^3}{800} \right) = -2.8233, \quad K_P = 0.0015 \end{aligned}$$

19. Determine the equilibrium yield of CH₃OH at 523 K and 1.0133×10^7 Pa in the reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}_{(\text{g})}$ if the initial mixture is stoichiometric; $K_{a,523} = 2.235 \times 10^{-3}$ (pressure is given in atmospheres).

Solution. Calculate K_a using Eq. (17.38):

$$K_a = K_f = \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{CO}} f_{\text{H}_2}^2} = \frac{x_{\text{CH}_3\text{OH}}}{x_{\text{CO}} x_{\text{H}_2}^2} \frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}} \gamma_{\text{H}_2}^2} P^{-2}$$

Find the values of γ_i by the method of corresponding states. The $\gamma = f(\pi, \tau)$ curve is given in the handbook:

Substance	$P_{\text{cr}} \times 10^{-5}$, Pa	π	T_{cr} , K	τ	γ
CH ₃ OH	79.54	1.27	513.2	1.02	0.55
CO	34.96	2.90	132.9	3.94	1.05
H ₂	12.96	7.82	33.3	15.71	1.06

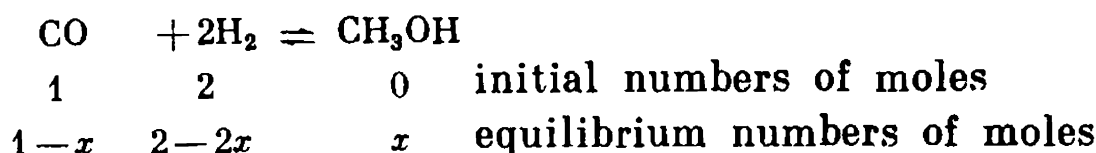
$$K_\gamma = \frac{0.55}{1.05 \times 1.06^2} = 0.466$$

$$K_a = 2.235 \times 10^{-3} = \frac{x_{\text{CH}_3\text{OH}}}{x_{\text{CO}} x_{\text{H}_2}^2} 0.466 \times 100^{-2}$$

Hence

$$\frac{x_{\text{CH}_3\text{OH}}}{x_{\text{CO}}x_{\text{H}_2}^2} = 47.96$$

Write the initial and equilibrium numbers of moles according to the equation of the reaction:



$$\sum_i n_i = 3 - 2x, \quad x_{\text{CH}_3\text{OH}} = \frac{x}{3 - 2x}, \quad x_{\text{CO}} = \frac{1 - x}{3 - 2x}, \quad x_{\text{H}_2} = \frac{2 - 2x}{3 - 2x},$$

$$\frac{x(3 - 2x)^3}{(3 - 2x)(1 - x)^3 \times 4} = \frac{x(3 - 2x)^2}{4(1 - x)^3} = 47.96$$

In order to calculate x , one must solve the third-degree equation. Find x by way of selection. The value of x cannot exceed unity and be negative: $1 > x > 0$. As can be determined from the above relation, $\frac{x(3 - 2x)^2}{(1 - x)^3} = 191.84$. If the root of the equation is substituted for x , the left-hand side will equal 191.84. If an arbitrary value is substituted for x , the left-hand side will be different from 191.84. Denoting $\frac{x(3 - 2x)^2}{(1 - x)^3}$ by A and using an arbitrary value of x gives different values of A . For instance, if $x = 0.900$, then $A = 1296$, if $x = 0.950$, then $A = 9196$. Consequently, A increases with x . If $x = 0.800$, then $A = 196.0$, and if $x = 0.790$, then $A = 172.0$. Linear interpolation between the last close values of A gives the value of the root of the equation:

$$\frac{(196.0 - 172.0) - 0.01}{(196.0 - 191.84) - y} = y = 0.0017$$

For $x = 0.7983$,

$$\frac{0.7983 \times 1.4034^2}{0.2017^3} = 192.6$$

which corresponds to the yield of methanol from 1 mole CO and 2 moles H₂:

$$0.7983 / (3 - 2 \times 0.7983) = 0.57 \text{ mole}$$

20. Determine the composition of an equilibrium mixture if the following composite reaction proceeds in the gas phase at 600 K:



The equilibrium constants of the reactions are $K_{P,(\text{I})} = 0.00154$ and $K_{P,(\text{II})} = 10.6$.

Solution. The methanol yielded by reaction (I) enters into reaction (II) to yield dimethyl ether and water. The two reactions proceed without any change in the number of moles, hence,

$$K_{P, (I)} = \frac{x_{\text{CH}_3\text{OH}} x_{\text{HCl}}}{x_{\text{CH}_3\text{Cl}} x_{\text{H}_2\text{O}}} = 0.00154$$

and

$$K_{P, (II)} = \frac{x_{\text{CH}_3\text{OCH}_3} x_{\text{H}_2\text{O}}}{x_{\text{CH}_3\text{OH}}^2} = 10.6$$

Denote the number of moles of HCl by x if the initial mixture consists of one mole of CH_3Cl and one mole of H_2O . Denote the number of moles of CH_3OCH_3 by y . Then, in the state of equilibrium, the system will contain $(1 - x)$ CH_3Cl , $(1 - x + y)$ H_2O , $(x - 2y)$ CH_3OH , x HCl , and y CH_3OCH_3 . Since the number of moles of the gaseous reaction products does not change, the numbers of moles are equal to molar fractions:

$$K_{P, (I)} = \frac{x(x - 2y)}{(1 - x)(1 - x + y)} = 0.00154, \quad K_{P, (II)} = \frac{y(1 - x + y)}{(x - 2y)^2} = 10.6$$

To find x and y , solve these two equations together. To facilitate the solutions express $\frac{x - 2y}{(1 - x + y)}$ from the second equation as $\frac{y}{10.6(x - 2y)}$ and substitute it into the first equation:

$$0.00154 = \frac{x}{1 - x} \frac{y}{10.6(x - 2y)}, \quad \frac{x}{1 - x} \frac{y}{x - 2y} = 0.016324$$

Solve the equations

$$\frac{x(x - 2y)}{(1 - x)(1 - x + y)} = 0.00154 \quad (\text{a})$$

and

$$\frac{xy}{(1 - x)(x - 2y)} = 0.016324 \quad (\text{b})$$

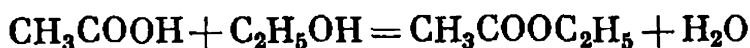
by the selection method. First find the range of possible values of x and y : $0 < x < 1$, $2y < x$, $y < 0.5x$, and $y < 0.5$. Given the values of x , find those of y using Eqs. (a) and (b):

x	y (a)	y (b)	Conclusion
0.1	0.04346	0.02060	y (a) differs significantly from y (b)
0.05	0.01094	0.00957	y (a) is close to y (b)
0.04	0.00222	0.008786	y (a) differs significantly from y (b)

An exact solution can be obtained by plotting $y(a) = f(x)$ and $y(b) = f(x)$. The coordinates of the point of intersection of the lines will represent the solutions of the equations: $x = 0.048$ and $y = 0.009$. The composition of the equilibrium mixture will then be as follows: 0.952 mole CH_3Cl , 0.961 mole H_2O , 0.030 mole CH_3OH , 0.009 mole CH_3OCH_3 , and 0.048 mole HCl .

Problems

1. Mixing one mole of acetic acid with one mole of ethanol initiates the reaction



When equilibrium is established, the reaction mixture contains $1/3$ of a mole of the acid, $1/3$ of a mole of the alcohol, $2/3$ of a mole of ether, and $2/3$ of a mole of water. Calculate the number of moles of ether in the reaction mixture in the state of equilibrium under the following conditions: (1) one mole of the acid in two moles of the alcohol; (2) one mole of the acid, one mole of the alcohol, and one mole of water; (3) one mole of ether and three moles of water; (4) one mole of the acid, one mole of the alcohol, one mole of ether, and one mole of water.

2. The equilibrium constant of the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ at 800 K is 4.12. A mixture of 20% CO and 80% H_2O is heated to 800 K. Determine the composition of the mixture in the state of equilibrium and the yield of hydrogen if 1 kg of water vapour is taken.

3. The equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$ at 717 K is 46.7. Determine the amount of dissociated HI after heating 1 mole HI to 717 K.

4. Determine the equilibrium constants K_P and K_c of the reaction of dissociation of I_2 when 1.513×10^{-3} mole of iodine is heated to 1073 K if its vapour occupies a volume of $249.3 \times 10^{-6} \text{ m}^3$ at $5.81 \times 10^4 \text{ Pa}$.

5. Calculate the pressure and degree of dissociation of N_2O_4 if, at 323 K, 1 mole N_2O_4 is in a vessel having a capacity of 0.075 m^3 . Determine the initial pressure of N_2O_4 (N_2O_4 dissociates in the reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$) if 1 mole N_2O_4 occupies, at 323 K, a vessel having a capacity of 0.125 m^3 . Once equilibrium is established in the vessel, the pressure is $3.485 \times 10^4 \text{ Pa}$.

6. Calculate the equilibrium constants K_P and K_c of the reaction $0.5 \text{ N}_2\text{O}_4 = \text{NO}_2$ if $\alpha = 0.533$, the pressure is $5.49 \times 10^4 \text{ Pa}$ at 323 K.

7. At 500 K, the equilibrium constant of the reaction $\text{PCl}_5 = \text{I}_2 + \text{PCl}_3$ is $K_P = 3.374 \times 10^4 \text{ Pa}$. Determine the degree of dissociation of PCl_5 at this temperature if the pressure in the state

of equilibrium is 8.106×10^4 Pa. At what total pressure in the system will the degree of dissociation of PCl_5 equal 70%?

8. At 900 K, the equilibrium constant of the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ is $K_c = 10^{11.51}$. The degree of dissociation of water vapour at this temperature and at 10.133×10^4 Pa is $10^{-7.575}$. Calculate the equilibrium constants K_P and K_c of the reaction $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ at the same temperature.

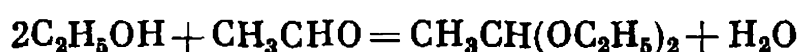
9. At 767 K and 9.899×10^4 Pa, nitrogen dioxide dissociates by 56.5% in the reaction $2\text{NO}_2 = 2\text{NO} + \text{O}_2$. Determine K_P and K_c and the pressure at which NO_2 dissociates at the same temperature by 80%.

10. At 375 K, the equilibrium constant of the reaction $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ is $K_c = 9.27$. Determine the concentration of SO_2Cl_2 in the state of equilibrium if the initial concentrations of SO_2 and Cl_2 are as follows: (1) $c_{\text{SO}_2} = c_{\text{Cl}_2} = 1$ kmole/ m^3 , (2) $c_{\text{SO}_2} = c_{\text{Cl}_2} = 2$ kmole/ m^3 , and (3) $c_{\text{SO}_2} = 1$ kmole/ m^3 , $c_{\text{Cl}_2} = 2$ kmole/ m^3 .

11. At 525 K, the equilibrium constant of the reaction $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ is $K_P = 1.780$. At what pressure should an equimolar mixture of Cl_2 and PCl_3 be taken for the pressure of PCl_5 to be 5×10^4 Pa in the state of equilibrium, $V = \text{const}$?

12. If 0.03 mole H_2 and 0.01 mole N_2 are injected into a vessel having a capacity of 1 m^3 , the pressure in it at 1000 K will be 18.127×10^4 Pa. Determine K_P and K_c of the reaction $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$ which will occur in the vessel.

13. A mixture of one mole of ethanol with 0.091 mole of acetaldehyde in the state of equilibrium at 298 K occupies a volume of $63 \times 10^{-3} \text{ m}^3$ with 90.72% of acetaldehyde entering into the reaction



Calculate the equilibrium constant K_c of this reaction.

14. Determine the equilibrium constant of the reaction $\text{I}_2 = 2\text{I}$ and the degree of dissociation at 973 K if m kg of iodine are placed in a volume of 10^{-3} m^3 where the equilibrium pressure is as follows:

$m \times 10^3, \text{ kg}$	0.1835	0.914	1.515	1.900
$P \times 10^{-5}, \text{ Pa}$	0.0632	0.3021	0.4963	0.6209

15. A bottle having a capacity of $3.4 \times 10^{-3} \text{ m}^3$ and containing $5 \times 10^{-3} \text{ kg}$ of phosgene is heated to 673 K, at which point the pressure in the bottle becomes equal to 10.133×10^4 Pa. Calculate the degree of dissociation of phosgene in the reaction $\text{COCl}_2 = \text{CO} + \text{Cl}_2$ and the equilibrium constants K_P and K_c under these conditions.

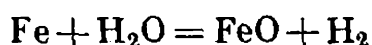
16. Calculate the degree of dissociation of phosgene at 673 K if $2.5 \times 10^{-3} \text{ kg}$ of this substance is placed in a bottle having a capacity of $3.4 \times 10^{-3} \text{ m}^3$ and $1 \times 10^{-3} \text{ kg}$ of chlorine is added to it. What

will the pressure in the bottle be? The equilibrium constant is $K_p = 4.99 \times 10^{-2}$ (atm).

17. Calculate the gas pressure after dissociation of phosgene at 673 K if 2.5×10^{-3} kg of this substance is placed in a bottle having a capacity of 3.4×10^{-3} m³ and 1×10^{-3} kg of nitrogen is added to it. The equilibrium constant is $K_p = 4.99 \times 10^{-2}$ (atm).

18. Determine the degree of dissociation of carbon dioxide in the reaction $2\text{CO}_2 = 2\text{CO} + \text{O}_2$ at 2273 K and 10.133×10^4 Pa if the equilibrium constant under these conditions is $K_p = 24.93$ Pa.

19. Iron and water vapour react as follows:



At 1000 K and 1.0133×10^5 Pa, the partial pressure of hydrogen is $P_{\text{H}_2} = 6.526 \times 10^4$ Pa. Calculate the equilibrium constant.

20. Determine the standard affinity for the reaction $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ if, at 873 K, $K_p = 2.86 \times 10^{-4}$ (Pa⁻¹).

21. At 633 K and 10.133×10^4 Pa, the degree of dissociation of HI is 20%. Calculate the standard affinity of gaseous iodine for hydrogen.

22. Will PCl_5 dissociate in a gas mixture containing PCl_3 , PCl_5 , and Cl_2 at 298 K at the following partial pressures (Pa): $P_{\text{PCl}_3} = 1.0133 \times 10^4$, $P_{\text{PCl}_5} = 0.5066 \times 10^4$, $P_{\text{Cl}_2} = 2.0266 \times 10^4$? Calculate the equilibrium constants with reference to $\Delta G_{f,298}^\circ$.

23. Calculate the affinity of iron for atmospheric oxygen, $P_{\text{O}_2} = 2.0266 \times 10^4$ Pa at 1000 K, if the equilibrium constant of the reaction $2\text{Fe} + \text{O}_2 = 2\text{FeO}$ at this temperature is 2.450×10^{20} .

24. Gaseous CO , Cl_2 , and COCl_2 are in 10 m³ tanks, their pressures being 2×10^4 , 3×10^4 , and 0.5×10^4 Pa, respectively. 10^{-5} mole CO and Cl_2 each have been transferred into a tank of the same capacity, containing an equilibrium mixture of the same gases, and 10^{-5} mole COCl_2 has been withdrawn from this tank. All processes have been conducted in an ideally reversible manner at 700 K. The equilibrium constant of the reaction at this temperature is 10.826. Determine the change in Gibbs' energy during the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$.

25. Determine the change in Gibbs' energy during the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ if no phosgene is withdrawn from the tank with the equilibrium mixture. The total pressure of the latter is 10^5 Pa.

26. The equilibrium constant of the reaction $2\text{H} = \text{H}_2$ can be written as

$$\log K_p (\text{Pa}) = \frac{22\,570}{T} - 1.504 \log T - 0.767$$

Determine the heat of the reaction at 800 K and derive the equation $\Delta H = f(T)$.

27. The equilibrium constant of the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ can be expressed as

$$\log K_c = \frac{24\,900}{T} - 1.335 \log T + 9.65 \times 10^{-5}T - 1.37 \times 10^{-7}T^2 + 1.08$$

while that of the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ can be written as

$$\log K_c = \frac{9586}{T} - 0.44 \log T + 2.16$$

Calculate K_c for the reaction $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ at 700 and 800 K, as well as ΔU at 800 K.

28. At 369 K, the pressure of dissociation (P_{NH_3}) of the compound $\text{LiCl} \cdot \text{NH}_3$ is 4.893×10^4 Pa, and at 382.2 K this pressure is 8.613×10^4 Pa. Calculate the heat of the reaction $\text{LiCl} \cdot \text{NH}_3 = \text{LiCl} + \text{NH}_3$ at a constant pressure and temperatures ranging from 369 to 382.2 K.

29. The vapour pressure over the system $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ at 303.2 K is 1.453×10^3 Pa, and at 299.3 K this pressure is 1.076×10^3 Pa. Calculate the heat of the reaction



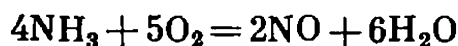
30. Depending on temperature, the heat of the reaction $2\text{C} + \text{H}_2 = \text{C}_2\text{H}_2$ varies almost linearly, equalling 225.2×10^3 J/mole at 700 K. The temperature coefficient of the heat of this reaction is -6.573 J mole $^{-1}$ K $^{-1}$. Determine the equilibrium constant of the reaction at 1500 K if $K_{P,700} = 1.353 \times 10^{-9}$.

31. The degree of dissociation of PCl_5 at 473 K and 1.0133×10^5 Pa is 0.485, and at 523 K and the same pressure it is 0.800. Calculate the mean heat of the reaction $\text{PCl}_3 + \text{Cl}_2 = \text{PCl}_5$ at $P = \text{const}$ and temperatures ranging from 473 K to 523 K.

32. The pressure of dissociation of MgCO_3 at 813 K is 9.959×10^4 Pa, and at 843 K it is 17.865×10^4 Pa. Calculate the heat of the reaction $\text{MgCO}_3 = \text{MgO} + \text{CO}_2$. Determine the temperature at which the MgCO_3 dissociation pressure will become equal to 1.0133×10^5 Pa.

33. The equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$ is 61.6 at 633 K and 41.7 at 718 K. Compare the mean heat of the reaction and affinity at 718 K. Calculate the change in entropy.

34*. Derive an equation of the $\log K_P = f(T)$ type for the ammonia oxidation reaction



if $K_P = 44.351$ at 1000 K. Calculate the equilibrium constant of the reaction at 1400 K.

35. Determine the temperature at which the pressure of CO_2 over CaCO_3 will be 1×10^5 Pa if, at 1035 K, the pressure is 13 332 Pa.

The heat of the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ at 1035 K is 167.91×10^3 J/mole. Assume that within a narrow temperature range the heat of the reaction is independent of temperature.

36*. Write the equation for the temperature dependence of the equilibrium constant K_P of the reaction $\text{CaCO}_{3(\text{calcite})} = \text{CaO} + \text{CO}_2$. Determine the pressure of CO_2 over CaCO_3 at 1200 K if, at 1035 K, this pressure is 13 332 Pa. To determine the temperature dependence of the reaction heat use the data given in the handbook.

37. Proceeding from the data given in the handbook, calculate the equilibrium constant of the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ at standard pressure and 298 K. Calculate the change in Gibbs' energy for this reaction at 298 K if the initial pressures are as follows (Pa): H_2 2.026×10^5 , Cl_2 1.013×10^5 , and HCl 0.103×10^5 . Remember that the process is ideally reversible.

38. The equilibrium constants of the reaction $\text{I}_2 = 2\text{I}$ at several temperatures are as follows:

$T, \text{ K}$	950	1050	1150	1250
$K_P \times 10^3$	1.134	7.316	33.833	127.122

Plot the $\log K_P = f(T^{-1})$ curve and determine the heat of the reaction in the above temperature range, using this curve. Derive an equation of the $\log K_P = f(T^{-1})$ type for the temperature range of 950 to 1250 K.

39. Determine the equilibrium constant of the reaction $2\text{C}_6\text{H}_5\text{CH}_3 = m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{C}_6\text{H}_6$ and the composition of the equilibrium mixture in molar fractions at 298 K and 1.0133×10^5 Pa. Use the necessary data from the handbook.

40. Use the Temkin-Shvartsman method to calculate ΔG° , K_P , and molar fractions of the equilibrium mixture for the reaction $2\text{C}_6\text{H}_5\text{CH}_3 = m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{C}_6\text{H}_6$ in the gas phase at 800 K and 1.0133×10^5 Pa.

41. Determine the equilibrium constant of the reaction $\text{A} + 2\text{B} = \text{AB}_2$ if the extinction coefficients of substances A and B are zero at a certain wavelength. The optical densities of the equilibrium mixtures at this wavelength are as follows:

$c_B, \text{ mole/litre}$	0.1	0.2	0.3	0.4	0.6	0.8	1.2	2.0
D	0.165	0.385	0.533	0.608	0.682	0.712	0.750	0.750

The concentration of substance A in all cases is 0.01 mole/litre. The cell is 5×10^{-2} m long.

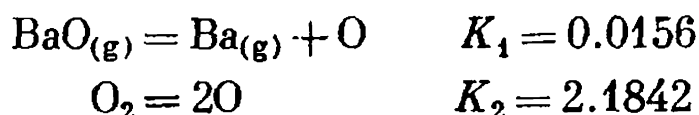
42. Determine the equilibrium constant of the reaction $\text{A} + 3\text{B} = \text{AB}_3$ if the extinction coefficients of substances A and B are zero at a certain wavelength. The intensity of the light passing through the cell with the solvent (a) and that of the light passing through the cell with the solution (b) at this wavelength are as follows for the equilibrium mixtures:

c_B , mole/litre	0.1	0.2	0.3	0.4	0.6	0.77	1.2	2.0
a	21.3	21.3	21.3	21.3	21.3	21.3	21.3	21.3
b	14.4	5.36	3.15	2.50	2.23	2.18	2.13	2.13

The concentration of substance A in all cases is 0.01 mole/litre, the cell being 1 cm long.

43. A certain amount of SO_3 was heated in a closed vessel to 727 K. Thermal dissociation has resulted in SO_2 and O_2 . Calculate (1) the initial pressure of SO_3 and (2) the total pressure of the equilibrium mixture if K_P of the reaction $\text{SO}_3 = \text{SO}_2 + 0.5\text{O}_2$ is 0.539. The equilibrium pressure of SO_2 is 4.05×10^4 Pa.

44. Calculate the constant of dissociation of BaO in the reaction $\text{BaO}_{(g)} = \text{Ba}_{(g)} + 0.5\text{O}_2$ at 4000 K if the equilibrium constants of the reactions are as follows:



45. Calculate the equilibrium constant of the reaction $\text{S} + \text{O}_2 = \text{SO}_2$ at 4000 K if the equilibrium constants K_P of the following reactions are as follows: $\text{SO}_2 = \text{S} + 2\text{O}$ (I), $K_I = 0.63$; $\text{O}_2 = 2\text{O}$ (II), $K_{II} = 2.184$.

46. The following equation has been derived for the reaction $\text{C}_6\text{H}_5\text{C}_2\text{H}_5_{(g)} + 3\text{H}_2 = \text{C}_6\text{H}_{11}\text{C}_2\text{H}_5_{(g)}$ at temperatures ranging from 485 to 565 K:

$$\log K_P (\text{Pa}) = \frac{9620}{T} - 33.058$$

Calculate the temperature at which this reaction will become possible if the initial gas mixture contains 10 moles of ethyl benzene, 50 moles of hydrogen, and 40 moles of ethyl cyclohexane. The total pressure of the initial gas mixture is 1.0133×10^5 Pa.

47*. Calculate the equilibrium constant of the reaction $0.5\text{H}_2 + 0.5\text{Cl}_2 = \text{HCl}$ at 900 K and 1.0133×10^5 Pa proceeding from the following rotational moments of inertia and vibrational frequencies:

Substance	HCl	Cl_2	H_2
$I \times 10^{47}$, kg m ²	2.612	116.3	0.459
$\omega_e \times 10^{-5}$, m ⁻¹	2.9894	0.5649	4.3966

The heat of the reaction in the ideal gaseous state at absolute zero is -92.140×10^3 J/mole.

48*. Calculate the equilibrium constant K_P of the reaction of thermal dissociation of iodine, $\text{I}_2 = 2\text{I}$, at 1274 K and 1.0133×10^5 Pa if $\Delta H_0^\circ = 148.766 \times 10^3$ J/mole, the vibrational frequency of the I_2 molecule is $\omega_e = 214.25 \times 10^2$ m⁻¹, and the moment of inertia is 750.1×10^{-47} kg m². The statistical weight of the zeroth electronic level of the iodine atom is 4, and that of the zeroth electronic level of the I_2 molecule is unity.

49*. Calculate the equilibrium constant K_P of the reaction $\text{NO} = 0.5\text{N}_2 + 0.5\text{O}_2$ at 1000 K and 1.0133×10^5 Pa if the rotational moments of inertia of the molecules, vibrational frequencies, and statistical weights of the zeroth electronic levels are as follows:

Substance	NO	N ₂	O ₂
$I \times 10^{47}, \text{kg m}^2$	16.43	14.01	19.34
$\omega_e \times 10^{-5}, \text{m}^{-1}$	1.9165	2.3594	1.5798
$g_{0,\text{el}}$	4	1	3

The heat of the reaction which proceeds in the ideal gaseous state at absolute zero is -90.761×10^3 J/mole.

50*. Calculate the equilibrium constant K_P of the reaction $\text{H}_2 + 0.5\text{S}_2 = \text{H}_2\text{S}$ at 1000 K and 1.0133×10^5 Pa if the moments of inertia of the molecules, vibrational frequencies, and statistical weights of the zeroth electronic levels are as follows:

Substance	H ₂ S		H ₂		S ₂
$I \times 10^{47}, \text{kg m}^2$	2.6674	3.1513	0.7187	0.459	94.88
$\omega_e \times 10^{-5}, \text{m}^{-1}$	2.7219	2.7394	1.2145	4.3966	0.7257
$g_{0,\text{el}}$	1		1		3

The H_2S molecule is nonlinear with symmetry C_{2v} , $\sigma = 2$. For H_2S , $\Delta H_0^\circ = -82.061$ kJ/mole.

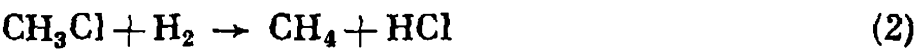
51*. Determine the equilibrium constant of the reaction $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$ at 1000 K and 1.0133×10^5 Pa if the moments of inertia of the molecules, vibrational frequencies, and heats of their formation in the ideal gaseous state at absolute zero are as follows:

Substance	$I \times 10^{47}, \text{kg m}^2$	$\omega_e \times 10^{-5}, \text{m}^{-1}$	$\Delta H_0^\circ, \text{kJ/mole}$
CO ₂	67.8336	1.3512	-393.229
		2.3964	
		0.6722	
H ₂	0.459	4.3966	0
H ₂ O	1.0296	3.8354	-238.906
	1.9674	3.9387	
	2.9970	1.6476	
CO	14.49	2.1700	-113.880

The CO_2 molecule vibrates in a double degenerate manner at a frequency of $0.6722 \times 10^5 \text{ m}^{-1}$.

52. Determine K_P of the reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$ at 1000 K, if the statistical sums of states are $Z_{\text{H}_2} = 3.5539 \times 10^7$, $Z_{\text{I}_2} = 3.2346 \times 10^{14}$, $Z_{\text{HI}} = 3.6320 \times 10^{11}$, and $\Delta H^\circ = -8.292 \text{ kJ}$.

53*. A reactor operating at a constant pressure contains 1 mole CH_2Cl_2 and 1 mole Cl_2 . The following reactions take place at 600 K:



The equilibrium constants of the reactions at 600 K are $K_{P_1} = 1.156 \times 10^8$ and $K_{P_2} = 8.8716 \times 10^6$. Determine the composition of the equilibrium mixture.

Multivariate Problems

1. Gaseous substances A and B react to yield gaseous product C: (1) express K_P and K_c in terms of an equilibrium amount of sub-

Variant	Reaction equation	Variant	Reaction equation
1	$A + B = \frac{1}{2} C$	13	$3A + \frac{1}{2} B = 3C$
2	$\frac{1}{2} A + B = C$	14	$3A + \frac{1}{2} B = 2C$
3	$3A + B = 2C$	15	$\frac{1}{2} A + \frac{1}{2} B = 3C$
4	$2A + 3B = 3C$	16	$\frac{1}{2} A + \frac{1}{2} B = C$
5	$2A + \frac{1}{2} B = 2C$	17	$A + 3B = 3C$
6	$3A + \frac{1}{2} B = C$	18	$3A + B = C$
7	$A + 2B = C$	19	$A + 2B = 2C$
8	$A + B = 3C$	20	$A + 2B = 3C$
9	$\frac{1}{2} A + B = 2C$	21	$A + B = 2C$
10	$\frac{1}{2} A + B = 3C$	22	$2A + 2B = C$
11	$2A + \frac{1}{2} B = 3C$	23	$2A + 2B = 3C$
12	$2A + 3B = 2C$	24	$3A + 3B = 2C$
		25	$\frac{1}{2} A + B = \frac{1}{2} C$

stance C, equal to x , if the initial substances A and B are taken in stoichiometric amounts at total pressure P of the equilibrium system and temperature T , K; (2) calculate K_P and K_c at 300 K if $P = 7.5 \times 10^4$ Pa and $x = 0.45$; (3) calculate the equilibrium amount of substance C at 3×10^4 Pa in the equilibrium system and at 300 K; (4) calculate the degree of transformation of substances A and B at 300 K.

2. A heterogeneous reaction proceeds at constant temperature T : (1) determine the standard affinity of substances A and B at 298 K;

Variant	Reaction	T , K	$P_1 \times 10^{-2}$, P_a	$P_2 \times 10^{-2}$, P_a	$P_3 \times 10^{-2}$, P_a	$V \times 10^3$, m ³
1	$C + 2H_2 = CH_4$	600	600	186	100	8
2	$C + 2H_2 = CH_4$	700	700	84	50	10
3	$C + 2H_2 = CH_4$	800	700	37	25	3
4	$C + 2H_2 = CH_4$	500	600	250	200	5
5	$2C + 2H_2 = C_2H_4$	1000	68 400	480	300	7
6	$2C + 2H_2 = C_2H_4$	2000	68 400	2050	1000	11
7	$2C + 2H_2 = C_2H_4$	1800	68 400	1290	800	9
8	$2C + O_2 = 2CO$	773	10	705	800	2
9	$2C + O_2 = 2CO$	873	100	572	500	4
10	$2C + O_2 = 2CO$	973	300	293	300	6
11	$2CuCl + H_2 = 2HCl + 2Cu$	673	500	361	500	4
12	$2CuCl + H_2 = 2HCl + 2Cu$	773	500	215	400	6
13	$Sn + 2H_2O = 2H_2 + SnO_2$	1073	50	690	800	3
14	$SnO_2 + 2H_2 = 2H_2O + Sn$	1073	500	152	200	8
15	$SnO_2 + 2H_2 = 2H_2O + Sn$	973	400	167	200	6
16	$SnO_2 + 2CO = 2CO_2 + Sn$	1173	700	580	100	2
17	$SnS + H_2 = H_2S + Sn$	783	10	745	900	5
18	$SnS + H_2 = H_2S + Sn$	1196	50	670	700	7
19	$PbS + H_2 = H_2S + Pb$	783	5	755	900	8
20	$PbS + H_2 = H_2S + Pb$	973	10	745	800	3
21	$PbS + H_2 = H_2S + Pb$	1273	50	654	700	5
22	$PbS + CO = COS + Pb$	1081	2	758	800	7
23	$PbS + CO = COS + Pb$	1370	10	747	800	9
24	$PbCl_2 + H_2 = 2HCl + Pb$	873	200	284	400	11
25	$PbCl_2 + H_2 = 2HCl + Pb$	1073	300	350	500	2

(2) calculate the equilibrium constants K_P and K_c of the reaction; (3) determine the amount of the reacted solid substance A if the volume of the system is V , m³, and the initial pressure of gas B is P_1 ,

the volume of the solid phase being ignored; (4) determine the change in Gibbs' energy relative to the onset of the reaction if the initial pressures of gaseous substances B and C are P_2 and P_3 , respectively, the reaction proceeding in an ideally reversible manner at temperature T , K.

3. g kg of substance A have been placed in a closed vessel having capacity V , m^3 . At temperature T , K, part of the water of crystallization has passed into the gas phase, and pressure P , Pa, has been

Vari- ant	g , kg	Substance A	V , m^3	T , K	P , Pa
1	0.047	$\text{LiBr} \cdot 2\text{H}_2\text{O}$	6	130	133.3
2	0.659	$\text{LiI} \cdot \text{H}_2\text{O}$	7	403	866.5
3	0.068	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	5	273	354.6
4	0.258	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	6	288	1190.4
5	0.057	$\text{NaCOOCH}_3 \cdot 3\text{H}_2\text{O}$	3	298	851.8
6	0.128	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	7	273	358.6
7	0.019	$\text{NaCOOCH}_3 \cdot 3\text{H}_2\text{O}$	6	273	120.0
8	0.890	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	8	298	2399.4
9	0.500	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	9	288	1161.0
10	0.210	$\text{NaCOOCH}_3 \cdot 3\text{H}_2\text{O}$	4	313	2492.7
11	0.612	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	7	298	2538.0
12	0.035	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	8	273	373.2
13	0.254	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	9	293	1767.6
14	0.018	$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	4	297	2439.4
15	0.856	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	10	343	1999.5
16	0.081	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	4	298	1940.8
17	3.010	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	10	298	2210.1
18	0.622	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	8	313	2826.0
19	1.495	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	9	309	2999.3
20	0.416	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	3	298	1037.1
21	1.174	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	8	303	2852.6
22	0.183	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	5	298	1135.7
23	0.208	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4	288	377.2
24	0.257	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3	298	733.2
25	1.190	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	5	313	2103.5

established in the vessel: (1) determine the amount of the water that has remained bound to substance A; (2) calculate the absolute amount of the solid phase in the equilibrium state of the system; (3) calculate K_P , K_c , ΔA_T° , and ΔG_T° of the reaction at temperature T , K.

Variant	Reaction (A)	K	T, K
1	$2H_2 + CO \rightleftharpoons CH_3OH$	$K_P = \frac{p_{CH_3OH}}{p_{H_2}^2 p_{CO}}$	800
2	$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$	$K_P = \frac{p_{H_2O}^4 p_{Cl_2}^2}{p_{HCl}^4 p_{O_2}}$	750
3	$\beta\text{-NH}_4Cl \rightleftharpoons NH_3 + HCl$	$K_P = p_{NH_3} p_{HCl}$	455
4	$2N_2 + 6H_2O \rightleftharpoons 4NH_3 + 3O_2$	$K_P = \frac{p_{NH_3}^4 p_{O_2}^3}{p_{N_2}^2 p_{H_2O}^6}$	1300
5	$4NO + 6H_2O \rightleftharpoons 4NH_3 + 5O_2$	$K_P = \frac{p_{NH_3}^4 p_{O_2}^5}{p_{NO}^4 p_{H_2O}^6}$	1000
6	$2NO_2 \rightleftharpoons 2NO + O_2$	$K_P = \frac{p_{NO}^2 p_{O_2}}{p_{NO_2}^2}$	700
7	$N_2O_4 \rightleftharpoons 2NO_2$	$K_P = \frac{p_{NO_2}^2}{p_{N_2O_4}}$	400
8	$Mg(OH)_2 \rightleftharpoons MgO + H_2O$	$K_P = p_{H_2O}$	500
9	$CaCO_3 \rightleftharpoons CaO + CO_2$	$K_P = p_{CO_2}$	1000
10	$Ca(OH)_2 \rightleftharpoons CaO + H_2O$	$K_P = p_{H_2O}$	500
11	$S_2 + 4H_2O \rightleftharpoons 2SO_2 + 4H_2$	$K_P = \frac{p_{SO_2}^2 p_{H_2}^4}{p_{S_2} p_{H_2O}^4}$	1000
12	$S_2 + 4CO_2 \rightleftharpoons 2SO_2 + 4CO$	$K_P = \frac{p_{SO_2}^2 p_{CO}^4}{p_{S_2} p_{CO_2}^4}$	900
13	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	$K_P = \frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2}}$	700
14	$SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$	$K_P = \frac{p_{SO_2Cl_2}}{p_{SO_2} p_{Cl_2}}$	400
15	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$K_P = \frac{p_{CH_4} p_{H_2O}}{p_{CO} p_{H_2}^3}$	1000
16	$4CO + 2SO_2 \rightleftharpoons S_2 + 4CO_2$	$K_P = \frac{p_{S_2} p_{CO_2}^4}{p_{CO}^4 p_{SO_2}^2}$	900
17	$COCl_2 \rightleftharpoons CO + Cl_2$	$K_P = \frac{p_{CO} p_{Cl_2}}{p_{COCl_2}}$	400

(Table concluded)

Variant	Reaction (A)	K	T, K
18	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$K_P = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}}$	1200
19	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	$K_P = \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4}$	1000
20	$2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$	$K_c = \frac{[\text{CO}]^2 [\text{O}_2]}{[\text{CO}_2]^2}$	700
21	$2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$	$K_P = \frac{p_{\text{CH}_4} p_{\text{CO}_2}}{p_{\text{CO}}^2 p_{\text{H}_2}^2}$	900
22	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	$K_c = \frac{[\text{C}_2\text{H}_4][\text{H}_2]}{[\text{C}_2\text{H}_6]}$	400
23	$\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	$K_P = \frac{p_{\text{C}_2\text{H}_4} p_{\text{H}_2\text{O}}}{p_{\text{C}_2\text{H}_5\text{OH}}}$	400
24	$\text{CH}_3\text{CHO} + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$	$K_P = \frac{p_{\text{C}_2\text{H}_5\text{OH}}}{p_{\text{CH}_3\text{CHO}} p_{\text{H}_2}}$	500
25	$\text{C}_6\text{H}_6 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$	$K_P = \frac{p_{\text{C}_6\text{H}_{12}}}{p_{\text{C}_6\text{H}_6} p_{\text{H}_2}^3}$	600

4. The temperature dependence of the equilibrium constant of reaction (A) is given by the equation

$$\log K_P = \frac{a}{T} + b \log T + cT + d$$

The values of the coefficients a , b , c , and d are given in the table on p. 313, and pressure is expressed in pascals: (1) determine the equilibrium constant of reaction (A) at T , K; (2) plot $\log K = f(T^{-1})$ at temperatures ranging from $(T - 100)$ to $(T + 100)$, K; (3) indicate how the equilibrium constant varies with increasing temperature; (4) determine the heat of reaction (A), ΔH_T° , at T , K; (5) compare the heat calculated as in (4) with that calculated using Kirchhoff's law at temperature T , K; (6) determine the standard affinity of the reactants at temperature T , K (see the table on pp. 311-312).

Variant	a	b	c	d
1	3 724	−9.1298	0.00308	3.401
2	5 750	−2.136	−0.000857	−4.710
3	−9 650	1.83	−0.00324	28.239
4	−66 250	−1.75	0	−10.206
5	−47 500	−1.75	0	−13.706
6	−5 749	1.75	−0.0005	7.899
7	−2 692	1.75	−0.00483	1.944
8	−4 600	0.623	−0.00102	17.776
9	−9 680	−1.385	−0.000219	17.756
10	−5 650	0.67	0.000414	9.616
11	−13 810	−0.877	0.00267	8.386
12	−23 000	4.34	−0.00162	2.567
13	10 373	1.222	0	−18.806
14	2 250	−1.75	0.000455	−7.206
15	9 874	−7.14	0.00188	−1.371
16	23 000	−4.34	0.0000002	−2.576
17	5 020	1.75	0	−3.748
18	−2 203	0	−0.0000516	2.3
19	7 674	−6.23	0.000906	−1.291
20	−29 500	1.75	−0.001215	−3.29
21	11 088	3.113	−0.0028524	−1.483
22	−6 365	2.961	−0.000766	−2.344
23	−1 485	7.54	−0.00425	7.006
24	1 522	5.42	−0.00229	−2.810
25	9 590	−9.9194	0.002285	−6.452

5. Proceeding from the values tabulated in the handbook, determine the following for a given reaction: (1) the standard affinity at temperature T , K; (2) the equilibrium yield of substance D at a total pressure of 1.0133×10^5 Pa and T , K if gaseous substances A and B have been injected into the reaction vessel in stoichiometric amounts; (3) the change in Gibbs' energy for the onset of the reaction if the initial partial pressures of the gases in the reaction mixture are P_A , P_B , P_C , and P_D and the reaction proceeds in an ideally reversible manner at temperature T , K.

Vari- ant	Reaction	A	B	C	D	P×10 ⁻⁴ Pa				T, K
						A	B	C	D	
1	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	H ₂	O ₂	—	H ₂ O	7	6	—	3	1000
2	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	H ₂	O ₂	—	H ₂ O	2	1	—	2	700
3	$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$	H ₂	Cl ₂	—	HCl	4	3	—	1.5	900
4	$2\text{HCl} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$	HCl	O ₂	Cl ₂	H ₂ O	4	3	1.5	1.5	1000
5	$2\text{HCl} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$	HCl	O ₂	Cl ₂	H ₂ O	1	4	2	1	700
6	$\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightleftharpoons \text{NH}_3$	N ₂	H ₂	—	NH ₃	10	15	—	10	600
7	$\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightleftharpoons \text{NH}_3$	N ₂	H ₂	—	NH ₃	20	10	—	10	800
8	$\frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}$	N ₂	O ₂	—	NO	2	1	—	0.3	2000
9	$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$	N ₂	O ₂	—	NO	4	1	—	1	1000
10	$\text{NO}_2 \rightleftharpoons \text{NO} + \frac{1}{2} \text{O}_2$	NO ₂	—	NO	O ₂	6	—	2	3	460

(Table concluded)

Vari- ant	Reaction	A	B	C	D	$P \times 10^{-4}$ Pa				T, K
						A	B	C	D	
11	$\text{NO}_2 \rightleftharpoons \text{NO} + \frac{1}{2} \text{O}_2$	NO_2	—	NO	O_2	3	—	3	3	400
12	$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	N_2O_4	—	—	NO_2	5	—	—	2	340
13	$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	N_2O_4	—	—	NO_2	2	—	—	2	320
14	$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3$	SO_2	O_2	—	SO_3	3	1	—	1.5	900
15	$\text{SO}_2 + \text{NO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}$	SO_2	NO_2	SO_3	NO	6	3	1.5	1.2	700
16	$\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$	PCl_3	Cl_2	—	PCl_5	3	6	—	2	500
17	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	CO	H_2O	CO_2	H_2	5	2	0.7	1.6	1000
18	$\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$	CO	Cl_2	—	COCl_2	2	3	—	0.5	900
19	$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	CO	H_2	—	CH_3OH	4	3	—	1.6	570
20	$\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2$	CO	O_2	—	CO_2	4	6	—	3	1000
21	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	CH_4	H_2O	CO	H_2	2	3	0.8	0.7	500
22	$3\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$	C_2H_4	—	C_6H_6	H_2	2	—	0.7	3	700
23	$\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$	C_2H_4	H_2	—	C_2H_6	7	8	—	3	780
24	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$	C_2H_4	H_2O	—	$\text{C}_2\text{H}_5\text{OH}$	3	2	—	1.2	480
25	$\text{C}_6\text{H}_6 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$	C_6H_6	H_2	—	C_6H_{12}	6	4	—	2	600

6. Proceeding from the values of $\left(\frac{G^\circ - H_0^\circ}{T}\right)$ and ΔH_0° given in the handbook, determine the equilibrium constant K_P of the reaction at temperature T , K.

Variant	Reaction	T , K
1	$\text{H}_2 + \text{F}_2 = 2\text{HF}$	600
2	$\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$	800
3	$\text{H}_2 + \text{Br}_2 = 2\text{HBr}$	800
4	$\text{H}_2 + \text{I}_2 = 2\text{HI}$	1000
5	$\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$	1500
6	$\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$	1000
7	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	800
8	$\text{C}_{(\text{graphite})} + \text{S}_2 = \text{CS}_2$	1000
9	$\text{N}_2 + \text{O}_2 = 2\text{NO}$	500
10	$\text{NO}_2 = \text{NO} + \frac{1}{2} \text{O}_2$	800
11	$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$	1200
12	$\text{S}_2 + 2\text{O}_2 = 2\text{SO}_2$	800
13	$\text{SO}_2 + \frac{1}{2} \text{O}_2 = \text{SO}_3$	1000
14	$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S}$	500
15	$\text{PCl}_3 + \text{Cl}_2 = \text{PCl}_5$	1000
16	$\text{C}_{(\text{graphite})} + 2\text{H}_2 = \text{CH}_4$	1500
17	$\text{C}_2\text{H}_2 + \text{H}_2 = \text{C}_2\text{H}_4$	500
18	$\text{C}_3\text{H}_6 + \text{H}_2 = \text{C}_3\text{H}_8$	800
19	$\text{C}_4\text{H}_8 = \text{C}_4\text{H}_6 + \text{H}_2$	1500
20	$\text{C}_4\text{H}_8 + \text{H}_2 = \text{C}_4\text{H}_{10}$	1000
21	$\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$	500
22	$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$	800
23	$\text{HCHO} + \text{H}_2 = \text{CH}_3\text{OH}$	500
24	$\text{CHCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{HCl}$	1000
25	$\text{CH}_3\text{Cl} + 2\text{Cl}_2 = \text{CHCl}_3 + 2\text{HCl}$	800

7. Using Le Chatelier's principle and Eqs. (17.3) and (17.30), determine how the equilibrium yield of the end products of the reaction will change if (a) the temperature is increased, (b) the temperature is decreased, (c) the pressure is increased, (d) the pressure is decreased, and (e) an inert gas is added.

Variant	Reaction	Variant	Reaction
1	$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$	14	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$
2	$\text{C} + \text{O}_2 = \text{CO}_2$	15	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} = \text{C}_2\text{H}_5\text{OH}_{(\text{liq})}$
3	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$	16	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$
4	$\text{C} + 2\text{H}_2 = \text{CH}_4$	17	$2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}_{(\text{liq})}$
5	$4\text{H}_2 + 2\text{SO}_2 = 4\text{H}_2\text{O}_{(\text{liq})} + \text{S}_{2(\text{s})}$	18	$\text{C}_2\text{H}_5\text{OH}_{(\text{liq})} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}_{(\text{g})}$
6	$2\text{C} + 2\text{H}_2 = \text{C}_2\text{H}_4$	19	$2\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O}_{(\text{g})} + 2\text{Cl}_2$
7	$\text{COCl}_2 = \text{CO} + \text{Cl}_2$	20	$2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$
8	$2\text{HI} = \text{H}_2 + \text{I}_2$	21	$2\text{NO} + \text{O}_2 = 2\text{NO}_2$
9	$2\text{CO} + \text{O}_2 = 2\text{CO}_2$	22	$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$
10	$2\text{H}_2\text{O}_{(\text{liq})} = 2\text{H}_2 + \text{O}_2$	23	$2\text{H}_2\text{O}_{(\text{g})} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$
11	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	24	$\text{NH}_4\text{Cl}_{(\text{s})} = \text{NH}_3 + \text{HCl}$
12	$\text{N}_2\text{O}_4 = 2\text{NO}_2$	25	$\text{CH}_3\text{CHO}_{(\text{g})} + \text{H}_2 = \text{C}_2\text{H}_5\text{OH}$
13	$2\text{NO}_2 = 2\text{NO} + \text{O}_2$		

8. Calculate the equilibrium constant K_P of the reaction at a given temperature T . Use the Temkin-Shvartsman method for the calculation.

Variant	Reaction	T , K
1	$2\text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{COCH}_3 + 3\text{H}_2 + \text{CO}$	400
2	$\text{CH}_4 + 2\text{PCl}_5 = 2\text{PCl}_3 + \text{CH}_2\text{Cl}_2 + 2\text{HCl}$	500
3	$\text{CH}_4 + \text{CO}_2 = \text{CH}_3\text{COOH}$	400
4	$2\text{H}_2 + \text{CO}_2 = \text{HCHO} + \text{H}_2\text{O}$	500
5	$\text{CO}_2 + \text{H}_2 = \text{HCOOH}$	400
6	$\text{CO} + \text{H}_2\text{O} = \text{HCOOH}$	400
7	$\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	500
8	$\text{C}_2\text{H}_6 + \text{CO} = \text{CH}_3\text{COCH}_3$	400
9	$\text{C}_2\text{H}_4 + \text{H}_2\text{O} = \text{CH}_3\text{CH}_2\text{OH}$	400
10	$\text{CH}_4 + 4\text{PCl}_5 = \text{CCl}_4 + 4\text{PCl}_3 + 4\text{HCl}$	400
11	$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$	500
12	$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	600
13	$\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$	900
14	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$	800
15	$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{H}_2$	700
16	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$	500
17	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$	700
18	$\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$	400
19	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$	500
20	$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$	600
21	$\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}$	800

(Table concluded)

Variant	Reaction	T, K
22	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$	900
23	$\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$	500
24	$\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$	500
25	$\text{S} + 2\text{CO}_2 = \text{SO}_2 + 2\text{CO}$	700

9. Determine the equilibrium partial pressures of all reactants and reaction products as well as the initial pressure of substance A if the equilibrium constant of its thermal dissociation at temperature T , K is known along with the total equilibrium pressure P of the mixture. The reaction proceeds in a closed vessel at temperature T , K.

Variant	Substance	Reaction	K_P	$P \times 10^{-4}$, Pa	T, K
1	H_2O	$\text{H}_2\text{O} = 2\text{H} + \text{O}$	2.096×10^{10}	1.0133	4000
2	H_2O	$\text{H}_2\text{O} = 2\text{H} + \text{O}$	0.991×10^{10}	2.0266	3900
3	H_2O	$\text{H}_2\text{O} = 2\text{H} + \text{O}$	4.271×10^{10}	3.0399	4100
4	SO_3	$\text{SO}_3 = \text{S} + 3\text{O}$	0.257×10^{15}	4.0532	3300
5	SO_3	$\text{SO}_3 = \text{S} + 3\text{O}$	1.200×10^{15}	5.0665	3400
6	SO_3	$\text{SO}_3 = \text{S} + 3\text{O}$	5.119×10^{15}	6.0800	3500
7	FNO	$\text{FNO} = \text{F} + \text{N} + \text{O}$	0.720×10^{10}	7.0931	3500
8	FNO	$\text{FNO} = \text{F} + \text{N} + \text{O}$	1.715×10^{10}	8.1064	3600
9	FNO	$\text{FNO} = \text{F} + \text{N} + \text{O}$	8.266×10^{10}	9.1197	3800
10	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	1.031×10^{15}	10.1330	3500
11	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	13.632×10^{15}	1.0133	3700
12	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	3.82×10^{15}	2.0266	3600
13	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	0.478×10^{15}	3.0399	4200
14	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	4.235×10^{15}	4.0532	4400
15	SOF_2	$\text{SOF}_2 = \text{S} + \text{O} + 2\text{F}$	11.726×10^{15}	5.0665	4500
16	C_2H_2	$\text{C}_2\text{H}_2 = 2\text{C}_{(\text{g})} + 2\text{H}$	0.477×10^{15}	6.0798	4300
17	C_2H_2	$\text{C}_2\text{H}_2 = 2\text{C}_{(\text{g})} + 2\text{H}$	3.808×10^{15}	7.0931	4500
18	C_2H_2	$\text{C}_2\text{H}_2 = 2\text{C}_{(\text{g})} + 2\text{H}$	25.596×10^{15}	8.1064	4700
19	SiF_4	$\text{SiF}_4 = \text{Si}_{(\text{g})} + 4\text{F}$	2.699×10^{20}	9.1197	4400
20	SiF_4	$\text{SiF}_4 = \text{Si}_{(\text{g})} + 4\text{F}$	11.281×10^{20}	10.1330	4500
21	SiF_4	$\text{SiF}_4 = \text{Si}_{(\text{g})} + 4\text{F}$	44.281×10^{20}	1.0133	4600
22	BiO_3	$\text{B}_2\text{O}_3 = 2\text{B} + 3\text{O}$	0.542×10^{20}	2.0266	4900
23	B_2O_3	$\text{B}_2\text{O}_3 = 2\text{B} + 3\text{O}$	2.066×10^{20}	3.0399	5000
24	B_2O_3	$\text{B}_2\text{O}_3 = 2\text{B} + 3\text{O}$	7.486×10^{20}	4.0532	5100
25	B_2O_3	$\text{B}_2\text{O}_3 = 2\text{B} + 3\text{O}$	25.830×10^{20}	5.0665	5200

CHAPTER 18

Electrolytic Conductance. Equilibrium in Electrolyte Solutions

Basic Equations and Symbols

Conductance is the reciprocal of resistance ($1/R$). Electrical conductivity is essentially the reciprocal of resistivity ρ :

$$r = \frac{1}{\rho} = \frac{1}{R_x} \frac{l}{S} \quad (18.1)$$

$$\frac{1}{\rho} = \kappa \quad (18.2)$$

where l is the length of the conductor, S is its cross section, and κ is conductivity.

The equivalent conductance λ is expressed in terms of conductivity

$$\lambda = \kappa V = \kappa/c \quad (18.3)$$

where V is dilution of the solution, and c is its concentration in g-equiv/litre. Dilution is basically the volume containing one gram-equivalent of the dissolved electrolyte.

Kohlrausch's equation (law of independent migration of ions) is

$$\lambda_0 = \lambda_+ + \lambda_- \quad (18.4)$$

where λ_0 is the equivalent conductance at infinite dilution, λ_+ and λ_- stand for the electrical conductivities (mobilities) of the cation and anion, respectively;

$$\lambda_+ = Fv_+^0, \quad \lambda_- = Fv_-^0 \quad (18.5)$$

where v_+^0 and v_-^0 stand for the absolute velocities of the ions, $\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$, and F is Faraday's constant.

The velocities v_+ and v_- of the ions depend on the field potential:

$$v_+ = v_+^0 \psi/l, \quad v_- = v_-^0 \psi/l \quad (18.6)$$

where ψ/l is the field intensity.

The absolute velocities of the ions differ. The fraction of the amount of electricity transferred by the fields of a given sign equals the transference number t_+ or t_- :

$$t_+ + t_- = 1$$

$$t_+ = \frac{v_+^0}{v_+^0 + v_-^0} = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\lambda_0}, \quad t_- = \frac{v_-^0}{v_+^0 + v_-^0} = \frac{\lambda_-}{\lambda_0} \quad (18.7)$$

The transference number of an ion is expressed as a change in the electrolyte concentration in the cathode (Δc_c) or anode (Δc_a) space:

$$t_+ = \frac{\Delta c_c}{\Delta c}, \quad t_- = \frac{\Delta c_a}{\Delta c} \quad (18.7a)$$

where Δc is the total decrease in the electrolyte concentration.

Kohlrausch's equation represents the relationship between conductance and concentration:

$$\lambda = \lambda_0 - A \sqrt{c} \quad (18.8)$$

A being a constant.

In the case of dissociation of a binary weak 1,1-valent electrolyte ($AB \rightleftharpoons A^+ + B^-$), the equilibrium constant is

$$K_c = \frac{[A^+][B^-]}{[AB]} \quad (18.9)$$

If the degree of dissociation is

$$\alpha = \frac{[A^+]}{c} = \frac{[B^-]}{c} = \frac{\lambda}{\lambda_0} \quad (18.10)$$

then the dissociation constant is

$$K_c = \alpha^2 c / (1 - \alpha) \quad (18.11)$$

For $K_c < 10^{-5}$ or $\alpha \ll 1$ it may be assumed that $K_c = \alpha^2 c$.

Substitution of α into Eq. (18.11) from Eq. (18.10) gives

$$K_c = \frac{\lambda^2 c}{\lambda_0 (\lambda_0 - \lambda)} \quad (18.12)$$

The temperature dependence of the dissociation constant is given by the equation

$$\frac{d \ln K_c}{dT} = \frac{\Delta H_{\text{diss}}}{RT^2} \quad (18.13)$$

whose integration results in the following relation:

$$\log \frac{K_{T_2}}{K_{T_1}} = - \frac{\Delta H_{\text{diss}}}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (18.14)$$

where ΔH_{diss} is the heat of dissociation. The work W of dissociation is determined from van't Hoff's isotherm equation:

$$W = - \Delta G^\circ = RT \ln K_c \quad (18.15)$$

in which ΔG° is the change in Gibbs' energy during dissociation.

In the case of strong electrolytes, activities should be substituted for concentrations in the thermodynamic equations. The activities of electrolytes are expressed in terms of molality and mean ionic activity coefficients (Table 4).

TABLE 4. Relationship Between Molality m , Mean Ionic Molality m_{\pm} , Activity a , and Mean Ionic Activity Coefficient γ_{\pm} for Different Electrolytes

Type of electrolyte valence	Electrolyte	Electrolyte activity, $a = (m_{\pm}\gamma_{\pm})^{\nu}$	Mean ionic activity, $a_{\pm} = \sqrt[\nu]{a}$
1-1, 2-2, 3-3	KCl, ZnSO ₄ , LaFe(CN) ₆	$m^2\gamma_{\pm}^2$	$m\gamma_{\pm}$
2-1, 1-2	CaCl ₂ , Na ₂ SO ₄	$4m^3\gamma_{\pm}^3$	$\sqrt[3]{4} m\gamma_{\pm}$
3-1, 1-3	AlCl ₃ , K ₃ Fe(CN) ₆	$27m^4\gamma_{\pm}^4$	$\sqrt[4]{27} m\gamma_{\pm}$
3-2	Al ₂ (SO ₄) ₃	$108m^5\gamma_{\pm}^5$	$\sqrt[5]{108} m\gamma_{\pm}$

The mean ionic molality m_{\pm} is related to the molality of the electrolyte as

$$m_{\pm} = m (\nu_+^{\nu} + \nu_-^{\nu})^{1/\nu} \quad (18.16)$$

where ν_+ and ν_- stand for the number of cations and anions, respectively, and ν is the total number of ions: $\nu = \nu_+ + \nu_-$.

The mean ionic activity coefficient γ_{\pm} is expressed in terms of ionic activity coefficients:

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu} \quad (18.17)$$

The mean ionic activity is

$$a_{\pm} = m_{\pm}\gamma_{\pm} \quad (18.18)$$

The total activity of an electrolyte is related to the mean ionic activity as follows:

$$a = (a_{\pm})^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \quad (18.19)$$

where a_+ and a_- stand for the activities of the respective ions;

$$a_+ = \gamma_+ m_+, \quad a_- = \gamma_- m_- \quad (18.20)$$

The ionic molalities are related to that of the electrolyte as

$$m_+ = \nu_+ m, \quad m_- = \nu_- m \quad (18.21)$$

The limiting Debye-Hückel equation relating the mean ionic activity coefficient to the ionic strength I of the solution takes the form

$$\log \gamma_{\pm} = -0.509 z_+ z_- \sqrt{I} \quad (18.22)$$

where z_+ and z_- are the charges of the cation and anion, respectively;

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (18.23)$$

where m_i is the molality of the i th ion in the solution, and z_i is the charge of the i th ion.

For a 1-1-valent electrolyte, Eq. (18.22) takes the form

$$\log \gamma_{\pm} = -509 \sqrt{m} \tag{18.24}$$

Equation (18.22) is applicable when $I \leq 0.001$. If the ionic strength of a solution does not exceed 0.1, the activity coefficients of individual like-charged ions are approximately equal (Table 5).

TABLE 5. Activity Coefficients of Ions

Ions	Activity coefficients at ionic strength I of solution					
	0.001	0.005	0.01	0.02	0.05	0.10
Singly charged	0.98	0.95	0.92	0.89	0.85	0.80
Doubly charged	0.77	0.65	0.58	0.50	0.40	0.30
Triply charged	0.73	0.55	0.47	0.37	0.28	0.21

The activities of substances dissolved in anhydrous solvents (amalgams, melts) are calculated using the following equations:

$$a_i = x_i \gamma_i \tag{18.25}$$

$$a_i = \frac{P_i}{P_i^0} \quad (P_i, P_i^0 \leq 1 \text{ atm}) \tag{18.26}$$

in which x_i is the molar fraction of the i th substance, γ_i is the rational activity coefficient, P_i is the pressure of the saturated i th substance over the solution (melt, amalgam), and P_i^0 is the saturated vapour pressure over the pure i th substance.

Exercises

1. For 0.01 N KCl, the resistivity $\rho = 709.22$ mho cm. Calculate the conductivity κ and equivalent conductance λ .

Solution. To calculate the conductivity use Eq. (18.2):

$$\kappa = \frac{1}{709.22} = 1.41 \times 10^{-3} \text{ mho cm}^{-1} = 0.141 \text{ mho m}^{-1}$$

According to Eq. (18.3), the equivalent conductance is

$$\lambda = \frac{0.141 \times 10^{-3}}{0.01} = 0.0141 \text{ mho g-equiv}^{-1} \text{ m}^2$$

2. Calculate the equivalent conductance of acetic acid at infinite dilution, at 298 K, if the conductivities of HCl, NaCOOCH₃, and NaCl are 0.0426, 0.0091, and 0.0126 mho g-equiv⁻¹ m², respectively.

Solution. Derive a system of equations according to Eq. (18.4):

$$\lambda_{0, \text{HCl}} = \lambda_{0, \text{H}^+} + \lambda_{0, \text{Cl}^-} = 0.0426 \quad (1)$$

$$\lambda_{0, \text{CH}_3\text{COONa}} = \lambda_{0, \text{Na}^+} + \lambda_{0, \text{CH}_3\text{COO}^-} = 0.0091 \quad (2)$$

$$\lambda_{0, \text{NaCl}} = \lambda_{0, \text{Na}^+} + \lambda_{0, \text{Cl}^-} = 0.0126 \quad (3)$$

According to Eq. (18.4) add up Eqs. (1) and (2) and subtract Eq. (3) from the sum:

$$\begin{aligned} \lambda_{0, \text{HCl}} + \lambda_{0, \text{CH}_3\text{COONa}} - \lambda_{0, \text{NaCl}} &= \lambda_{\text{H}^+} + \lambda_{\text{CH}_3\text{COO}^-} \\ &- \lambda_{0, \text{CH}_3\text{COOH}} = 0.0426 + 0.0091 - 0.0126 = 0.0391 \text{ mho g-equiv}^{-1} \text{ m}^2 \end{aligned}$$

3. At 298.2 K, the cation transference number for an infinitely dilute solution of NH_4Cl is $t_+ = 0.491$. Calculate the mobility and absolute velocity of anion Cl^- ; $\lambda_{0, \text{NH}_4\text{Cl}} = 0.0150 \text{ mho g-equiv}^{-1} \text{ m}^2$.

Solution. According to Eq. (18.7),

$$\lambda_- = \lambda_0 (1 - t_+) = 0.015 (1 - 0.491) = 0.00763 \text{ mho g-equiv}^{-1} \text{ m}^2$$

To calculate the absolute velocity v_-^0 , use Eq. (18.5):

$$v_-^0 = \frac{0.00763}{9.65 \times 10^4} = 7.91 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$$

4. During electrolysis of an AgNO_3 solution, 0.5831 g of silver was deposited on the cathode, the AgNO_3 loss from the cathode space being 2.85×10^{-3} mole. Determine the transference numbers t_- and t_+ for AgNO_3 .

Solution. The loss of silver from the cathode space (Δc_c) and the total loss of AgNO_3 from the solution (Δc), corresponding to the amount of silver deposited on the cathode, must be expressed in the same units. Find the number of moles of silver deposited on the cathode:

$$\Delta c = \Delta n = \frac{m}{M} = \frac{0.5831}{107.9} = 5.4 \times 10^{-3} \text{ mole}$$

Substitution of the result into Eq. (18.7a) gives

$$t_- = \frac{2.85 \times 10^{-3}}{5.4 \times 10^{-3}} = 0.528, \quad t_+ = 1 - t_- = 0.472$$

5. Calculate the mean ionic molality, total activity of the electrolyte, and the activities of ions SO_4^{2-} and Cr^{3+} for 0.1 m $\text{Cr}_2(\text{SO}_4)_3$ at 298 K.

Solution. Calculate the mean ionic molality using Eq. (18.16):

$$m_{\pm} = (2^2 \times 3^3)^{1/5} \times 0.1 = 0.255$$

To calculate the mean ionic activity use Eq. (18.18):

$$\gamma_{\pm} = 0.0458 \text{ (handbook)}, \quad a_{\pm} = 0.255 \times 0.0458 = 0.0177$$

Use Eq. (18.19) to calculate the total activity a of the electrolyte:

$$a = (0.0177)^5 = 2.17 \times 10^{10}$$

To calculate the ionic molalities $m_{\text{Cr}^{3+}}$ and $m_{\text{SO}_4^{2-}}$ use Eqs. (18.21):

$$m_{\text{Cr}^{3+}} = 0.1 \times 3 = 0.3, \quad m_{\text{SO}_4^{2-}} = 0.1 \times 2 = 0.2$$

and calculate the activities of the anion and cation using Eqs. (18.20):

$$a_{\text{Cr}^{3+}} = 0.3 \times 0.0458 = 0.0137$$

$$a_{\text{SO}_4^{2-}} = 0.2 \times 0.0458 = 0.0092$$

6. Determine the ionic strength I of a solution containing 0.001 mole H_2SO_4 and 0.002 mole MgSO_4 per 1000 g of water at 298 K.

Solution. According to Eq. (18.23),

$$I = \frac{1}{2} (m_{\text{H}^+} z_+^2 + m_{\text{SO}_4^{2-}} z_-^2 + m_{\text{Mg}^{2+}} z_+^2 + m_{\text{SO}_4^{2-}} z_-^2)$$

To determine the ionic molalities use Eqs. (18.21). Then, the ionic strength will be

$$I = \frac{1}{2} (2 \times 0.001 \times 1^2 + 0.001 \times 2^2 + 0.002 \times 2^2 + 0.002 \times 2^2) = 0.011$$

7. Calculate the mean ionic activity coefficients γ_{\pm} for 0.01 and 0.0001 M NaCl solutions and compare the results with the experimental data (see the handbook).

Solution. Calculate the mean ionic activity coefficients using Eq. (18.24):

$$\log \gamma_{\pm} = -0.509 \sqrt{0.01} = -0.0509, \quad \gamma_{\pm} = 0.888$$

$$\log \gamma_{\pm} = -0.509 \sqrt{0.0001} = -0.016, \quad \gamma_{\pm} = 0.963$$

m	0.01	0.001
$\gamma_{\pm}, \text{calc}$	0.888	0.963
$\gamma_{\pm}, \text{exper}$	0.903	0.965

The above data indicates that the limiting equation (18.22) produces reliable results only at $I \leq 10^{-3}$.

8. Calculate the degree of dissociation of water at 298 K, proceeding from the conductivity of water, its density, and ionic mobility.

Solution. Find the conductivity of water and the equivalent conductances of ions H^+ and OH^- at infinite dilution in the handbook;

$$\kappa = 6.33 \times 10^{-8} \text{ mho cm}^{-1}$$

$$\lambda_{\text{H}^+} = 349.8 \text{ mho mole}^{-1} \text{ cm}^2$$

$$\lambda_{\text{OH}^-} = 198.3 \text{ mho mole}^{-1} \text{ cm}^2$$

Determine the concentration of water from its density (use the handbook):

$$c_{\text{H}_2\text{O}} = \frac{d \cdot 1000}{M} = \frac{0.997}{18} = 55.39 \text{ mole/litre}$$

To determine the degree of dissociation of water use the equation

$$\alpha = \frac{\kappa}{c(\lambda_{\text{H}^+} + \lambda_{\text{OH}^-})} = \frac{6.33 \times 10^{-8}}{55.39 \times 10^{-3} (349.8 + 198.3)} = 2.09 \times 10^{-9}$$

9. Calculate the degree of dissociation and pH of $1.6 \times 10^{-4} \text{ M}$ CH_3COOH at 298 K. The dissociation constant of CH_3COOH is $K_c = 1.75 \times 10^{-5}$.

Solution. Calculate the degree of dissociation of CH_3COOH using Eq. (18.11):

$$1.75 \times 10^{-5} = \frac{\alpha^2 1.6 \times 10^{-4}}{(1 - \alpha)}$$

Formulate the quadratic equation

$$1.6\alpha^2 + 0.175\alpha - 0.175 = 0$$

whose solution gives $\alpha = 0.28$. To find the hydrogen ion concentration use Eq. (18.10):

$$[\text{H}^+] = c\alpha = 1.6 \times 10^{-4} \times 0.28 = 4.48 \times 10^{-5}$$

consequently,

$$\text{pH} = -\log 4.48 \times 10^{-5} = 4.34$$

10. The constant of dissociation of ammonium hydroxide at 298 K is 1.77×10^{-5} . Calculate the concentration of ions OH^- and H^+ as well as pH of 0.1 M NH_4OH .

Solution. To calculate the OH^- concentration use Eq. (18.9). Assume that the concentration of NH_4OH is virtually equal to the initial one (at $K_c \leq 10^{-5}$). Then,

$$[\text{OH}^-] = [\text{NH}_4^+] = \alpha c = \sqrt{K_c c} = \sqrt{1.77 \times 10^{-5} \times 0.1} = 1.33 \times 10^{-3} \text{ mole/litre}$$

Determine the hydrogen ions concentration from the ionic product of water:

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} = 1.008 \times 10^{-14} \text{ (handbook)}$$

Assume that the activities of H^+ and OH^- equal their concentrations:

$$a_{\text{H}^+} = c_{\text{H}^+} = \frac{1.008 \times 10^{-14}}{1.33 \times 10^{-3}} = 0.76 \times 10^{-11} \text{ mole/litre}$$

Calculate the pH value:

$$\text{pH} = -\log c_{\text{H}^+} = -\log 7.6 \times 10^{-10} = 11.12$$

11. Calculate the concentration of ions OH^- in a 0.1 M NH_4OH solution containing 1 mole/litre NH_4Cl . How will the pH of the NH_4OH solution change when NH_4Cl is added to it? Salt NH_4Cl dissociates completely.

Solution. Calculate the OH^- concentration using Eq. (18.9). Assume that the NH_4OH concentration is virtually equal to the initial one, $[\text{NH}_4\text{OH}] = 0.1$ mole/litre, and that the concentration of the NH_4^+ ion equals that of NH_4Cl because $\alpha_{\text{NH}_4\text{Cl}} = 1$. Hence, $[\text{NH}_4^+] = 1$ mole/litre. Find the dissociation constant of NH_4OH in the handbook. Substitute the numerical values into Eq. (18.9):

$$1.77 \times 10^{-5} = \frac{[\text{OH}^-] \times 1}{0.1}, \quad [\text{OH}^-] = 1.77 \times 10^{-6}$$

As a result of addition of NH_4Cl , the OH^- concentration goes down and, consequently, the pH of the solution decreased.

12. It is known that for 0.005 and 0.05 m aqueous solutions of sulphuric acid, at 298 K, the pH values are 2.1 and 1.2, respectively. Calculate the pH value of this solution, proceeding from the mean ionic activity coefficients and those of individual ions.

Compare the results with the experimental values and draw the appropriate conclusions.

Solution. To calculate pH, determine the activity of the hydrogen ion. Calculate the ionic strength of the solution using Eq. (18.23):

$$I = \frac{1}{2} (2 \times 0.005 \times 1^2 + 0.005 \times 2^2) = 0.015$$

Find γ_{\pm} in the handbook. Calculate the activities a_{\pm} and a_{H^+} using Eqs. (18.18) and (18.20). Tabulate the input data and the calculation results:

m , mole/1000 g	pH_{exper}	γ_{\pm}	I	γ_{H^+}	pH_{calc}	
					$-\log \gamma_{\pm} m_{\pm}$	$-\log \gamma_{+} m_{+}$
0.005	2.1	0.639	0.015	0.905	2.19	2.04
0.05	1.2	0.34	> 0.1	—	1.10	—

Comparison of the calculated pH values with the experimental ones indicates that the calculation gives only approximate values. The agreement between the calculated and experimental values is better in the case of a more dilute solution.

13. Calculate the solubility product for $\text{Ca}(\text{OH})_2$ at 298 K. The solubility of calcium hydroxide is 0.155 g/100 g of water.

Solution. To calculate the activities of ions use Eq. (18.20). The molality of the saturated solution is

$$m = \frac{0.155 \times 10}{M} = \frac{1.55}{74.1} = 0.0209 \text{ mole/1000 g}$$

Calculate the mean ionic activity coefficients using Eq. (18.22). But first find the ionic strength of the solution with the aid of Eq. (18.23):

$$I = \frac{1}{2} (0.0209 \times 2^2 + 2 \times 0.0209 \times 1) = 6.27 \times 10^{-2}$$

Substitute the result into Eq. (18.22):

$$\log \gamma_{\pm} = -0.509 \times 1 \times 2 \sqrt{6.27 \times 10^{-2}} = -0.255$$

and

$$\gamma_{\pm} = 0.556$$

Calculate the solubility product:

$$\begin{aligned} \text{SP} &= m_{\text{Ca}^{2+}} \gamma_{\pm} (2m_{\text{OH}^{-}} \gamma_{\pm})^2 = 4m^3 \gamma_{\pm}^3 = 4(0.0209)^3 \times 0.516^3 \\ &= 6.28 \times 10^{-6} \text{ (mole/litre)}^3 \end{aligned}$$

14. Calculate the solubility of CuCl at 298 K in pure water and in 0.025 M MgSO_4 . Use the solubility product for CuCl .

Solution. Calculate the solubility of CuCl assuming that the concentration of the electrolyte is very low because CuCl dissociates completely and the ionic activity coefficients equal unity. Hence,

$$[\text{CuCl}] = [\text{Cu}^+] = \sqrt{\text{SP}}$$

$$\text{SP} = 3.2 \times 10^{-7} \text{ (mole/litre)}^2 \text{ (handbook)}$$

$$[\text{CuCl}] = \sqrt{3.2 \times 10^{-7}} = 5.65 \times 10^{-4} \text{ mole/litre}$$

While calculating the solubility of CuCl in the MgSO_4 solution, do not assume that the activity coefficients equal unity because $[\text{MgSO}_4] = 0.025$. Then,

$$[\text{CuCl}] = \sqrt{\text{SP}/\gamma_{\text{Cu}^+} \gamma_{\text{Cl}^-}}$$

To calculate the activity coefficients use Eq. (18.22). Use Eq. (18.23) to calculate the ionic strength of the solution:

$$I = \frac{1}{2} (0.025 \times 2^2 + 0.025 \times 2^2) = 0.1$$

Find the activity coefficients for the doubly charged ions in Table 5: $\gamma_{\text{Mg}^{2+}} = \gamma_{\text{SO}_4^{2-}} = 0.3$. Calculate the solubility of CuCl :

$$[\text{CuCl}] = \sqrt{3.2 \times 10^{-7}/0.3 \times 0.3} = 1.88 \times 10^{-4} \text{ mole/litre}$$

15. Calculate the heat of neutralization at 298 K using the tables of standard thermodynamic values for ions in aqueous solutions of electrolytes from the handbook.

Solution. The heat of neutralization equals that of the reaction $\text{H}_{(\text{aq})}^+ + \text{OH}_{(\text{aq})}^- = \text{H}_2\text{O}_{(\text{liq})}$ proceeding in a hypothetical finitely dilute solution. To calculate ΔH_{neutr} use the following equations:

$$\Delta H_{\text{neutr}} = \Delta H_{f, \text{H}_2\text{O}}^\circ - \Delta H_{f, \text{H}^+}^\circ - \Delta H_{f, \text{OH}^-}^\circ, \quad \Delta H_{f, \text{H}^+}^\circ = 0$$

$$\Delta H_{f, \text{OH}^-}^\circ = -229.94 \text{ kJ/mole}$$

$$\Delta H_{f, \text{H}_2\text{O}}^\circ = -285.84 \text{ kJ/mole (handbook)}$$

$$\Delta H_{\text{neutr}}^\circ = -285.84 - (-229.94) = -55.94 \text{ kJ/mole}$$

16. Calculate the ionic product of water, $K_w = a_{\text{H}^+}a_{\text{OH}^-}$, at 298 K, using the tabulated standard thermodynamic values for ions in aqueous solutions of electrolytes, $\Delta G_{\text{H}_2\text{O}}^\circ = -237.25 \text{ kJ/mole}$.

Solution. The equilibrium constant of the water dissociation reaction $\text{H}_2\text{O}_{(\text{liq})} \rightleftharpoons \text{H}^+ + \text{OH}^-$ is expressed in terms of activities:

$$K_a = \frac{a_{\text{H}^+}a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{K_w}{a_{\text{H}_2\text{O}}}$$

Since the concentration of ions H^+ and OH^- in water is vanishingly small, $x_{\text{H}_2\text{O}} = 1 = a_{\text{H}_2\text{O}}$ or $K_w = K_a$. Determine the dissociation constant from the equations

$$\Delta G_{\text{diss}}^\circ = -RT \ln K_a$$

$$\Delta G_{\text{diss}}^\circ = \Delta G_{\text{H}^+}^\circ + \Delta G_{\text{OH}^-}^\circ - \Delta G_{\text{H}_2\text{O}}^\circ$$

$$\Delta G_{\text{H}^+}^\circ = 0, \quad \Delta G_{\text{OH}^-}^\circ = -157.30 \text{ kJ/mole (handbook)}$$

$$\Delta G_{\text{diss}}^\circ = -157.30 - (-237.25) = 79.950 \text{ kJ/mole}$$

$$\log K_a = -79.95 \times 10^3 / 2.3 \times 8.314 \times 298.15 = -14.023$$

$$K_a = K_w = 0.95 \times 10^{-14}$$

17. The temperature dependence of the dissociation constant

$$\log K_a = -\frac{1342.85}{T} + 5.2743 - 0.0152T$$

is given for the formic acid dissociation reaction $(\text{HCOOH})_{\text{aq}} = \text{H}^+ + \text{HCOO}^-$. Calculate the heat of dissociation, ΔH_{diss} , and that of neutralization, ΔH_{neutr} , of formic acid in a dilute aqueous solution.

Solution. According to the equation,

$$\Delta H_{\text{diss}} = \left(\frac{d \ln K_a}{d} \right) RT^2$$

Proceed to the natural logarithm:

$$\ln K_a = -2.3 \times 1342.85/T + 2.3 \times 5.2743 - 2.3 \times 0.0152T$$

and take the derivative $\frac{d \ln K_a}{dT}$:

$$\frac{d \ln K_a}{dT} = 2.3 \times 1342.85/T^2 - 2.3 \times 0.0152$$

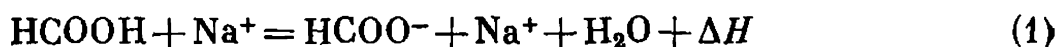
Multiply the derivative by RT^2 , and this will give

$$\Delta H_{\text{diss}} = 2.3R \times 1342.85 - 2.3R \times 0.0152T^2$$

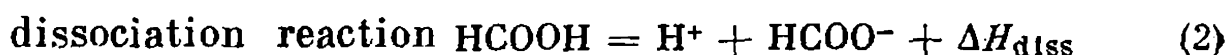
Consequently,

$$\Delta H_{\text{diss}} = -133.15 \text{ J/mole}$$

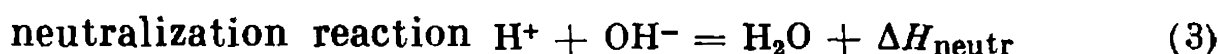
The thermochemical equation of the formic acid neutralization reaction,



can be written as the sum of the following two reaction equations:



and



Summing up Eqs. (2) and (3) gives Eq. (1) and indicates that $\Delta H = \Delta H_{\text{diss}} + \Delta H_{\text{neutr}}$. Since $\Delta H_{\text{diss}} = -133.15 \text{ kJ/mole}$, $\Delta H_{\text{neutr}} = -55.94 \text{ kJ/mole}$. Hence, the heat of neutralization of formic acid in a dilute aqueous solution will be $\Delta H = -56.072 \text{ kJ/mole}$.

18. Calculate the entropy of the dissociation reaction, ΔS_{diss} , at 298 K, and that of ion HCOO^- if the entropy of HCOOH in a dilute aqueous solution is $S_{(\text{HCOOH})_{\text{aq}}}^\circ = 163.8 \text{ J/mole}$, and the temperature dependence of the formic acid dissociation constant is given by the equation

$$\log K_a = -\frac{1342.85}{T} - 0.0152T + 5.2743$$

Solution. Use Eq. (18.15) to calculate ΔG_{diss}

$$\begin{aligned} \Delta G_{\text{diss}} &= +1342.85 \times 2.3R - 5.2745 \times 2.3RT + 0.0152 \times 2.3RT^2 \\ &= 2560492 - 100.57T + 0.291T^2 \end{aligned}$$

Then taking the derivative with respect to temperature, find ΔS_{diss} :

$$-\Delta S_{\text{diss}} = \left(\frac{\partial \Delta G}{\partial T} \right)_P = -100.57 + 2 \times 0.291T$$

and at 298 K,

$$\Delta S_{\text{diss}} = 100.57 - 2 \times 0.291 \times 298 = -72.87 \text{ J mole}^{-1} \text{ K}^{-1}$$

Calculate the entropy of ion HCOO^- :

$$\Delta S_{\text{diss}} = S_{\text{HCOO}^-}^\circ + S_{\text{H}^+}^\circ - S_{(\text{HCOOH})\text{aq}}^\circ$$

Since $S_{\text{H}^+}^\circ = 0$, then $S_{\text{HCOO}^-}^\circ = S_{\text{HCOOH}} + \Delta S_{\text{diss}} = 163.29 - 72.87 = 90.42 \text{ J mole}^{-1} \text{ K}^{-1}$.

19. Determine the temperature at which the dissociation of formic acid in an aqueous solution is maximum. The temperature dependence of the HCOOH dissociation constant takes the form

$$\log K_a = -\frac{1342.85}{T} + 5.2743 - 0.0152T$$

Solution. Find the coordinates of the extremum on the $\log K_{\text{diss}} = f(T)$ curve:

$$\frac{d \ln K_a}{dT} = 3098.55/T^2 - 0.035$$

Consequently, at the extremum (which is a maximum because $\frac{\partial^2 \ln K_a}{\partial T^2} < 0$),

$$T_{\text{max}} = \sqrt{3098.55/0.035} = 297 \text{ K}$$

The dissociation of formic acid is maximum at 297 K.

20. Calculate the solubility product SP for Ag_2CO_3 . Base the calculation on the standard thermodynamic properties of inorganic substances, whose values are given in the handbook.

Solution. According to the heterogeneous equilibrium condition (18.1), $\mu_i^s = \mu_i^{\text{sat.sol.}}$,

$$\Delta \bar{G}_{\text{Ag}_2\text{CO}_3(\text{sat.sol.})} = \Delta G_{\text{Ag}_2\text{CO}_3(\text{s})}^\circ \quad (1)$$

We find in the handbook that

$$\Delta G_{\text{Ag}_2\text{CO}_3(\text{s})}^\circ = -437.79 \text{ kJ/mole}$$

$$\Delta \bar{G}_{\text{Ag}_2\text{CO}_3(\text{sat.sol.})} = \Delta G_{\text{Ag}_2\text{CO}_3(\text{inf.dil.})}^\circ + RT \ln a_{\text{Ag}_2\text{CO}_3} \quad (2)$$

$$\Delta G_{\text{Ag}_2\text{CO}_3(\text{inf.dil.})}^\circ = 2\Delta G_{\text{Ag}^+}^\circ + \Delta G_{\text{CO}_3^{2-}}^\circ \quad (3)$$

$$a_{\text{Ag}_2\text{CO}_3} = a_{\text{Ag}^+}^2 a_{\text{CO}_3^{2-}} = \text{SP} \quad (4)$$

$$\Delta G_{\text{Ag}^+}^\circ = 77.21 \text{ kJ/mole}$$

$$\Delta G_{\text{CO}_3^{2-}}^\circ = -528.48 \text{ kJ/mole (handbook)}$$

Substitution of the numerical values into Eqs. (1) through (3) gives

$$-437.79 = 2 \times 77.21 - 528.48 + 2.3 \times 8.314 \times 298 \log \text{SP}$$

$$\log \text{SP} = \frac{-63.73 \times 10^3}{2.3 \times 8.314 \times 298} = -11.16$$

$$\text{SP} = 6.92 \times 10^{-12} \text{ (mole/litre)}^3$$

21. Calculate the partial pressure of 6 *m* hydrochloric acid at 298 K, proceeding from the standard values of Gibbs' energy and the mean ionic activity coefficients.

Solution. According to the heterogeneous equilibrium condition,

$$\mu_{\text{HCl(g)}} = \mu_{\text{HCl(sol)}} \quad (1)$$

$$\mu_{\text{HCl(g)}} = \mu_{\text{HCl(g)}}^{\circ} + RT \ln a_{\text{HCl(g)}} \quad (2)$$

$$\mu_{\text{HCl(sol)}} = \mu_{\text{HCl(inf.dil.)}}^{\circ} + RT \ln a_{\text{HCl(sol)}} \quad (3)$$

$$a_{\text{HCl(g)}} = P_{\text{HCl}}/1 \quad (4)$$

$$a_{\text{HCl(sol)}} = m^2 \gamma_{\pm}^2 \quad (5)$$

According to Eqs. (1) through (5),

$$\mu_{\text{HCl(g)}}^{\circ} + RT \ln P_{\text{HCl}} = \mu_{\text{HCl(inf.dil.)}}^{\circ} + RT \ln m^2 \gamma_{\pm}^2$$

and

$$\log P_{\text{HCl}} = \frac{\mu_{\text{HCl(inf.dil.)}}^{\circ} + RT \ln m^2 \gamma_{\pm}^2 - \mu_{\text{HCl(g)}}^{\circ}}{2.3RT}$$

$$\begin{aligned} \mu_{\text{HCl(inf.dil.)}}^{\circ} &= \Delta G_{\text{HCl(inf.dil.)}}^{\circ} = \Delta G_{\text{H}^+}^{\circ} + \Delta G_{\text{Cl}^-}^{\circ} \\ &= 0 + (-131.35) = -131.35 \text{ kJ/mole (handbook)} \end{aligned}$$

$$\mu_{\text{HCl(g)}}^{\circ} = \Delta G_{\text{HCl(g)}}^{\circ} = -95.36 \text{ kJ/mole (handbook)}$$

$$\gamma_{\pm} = 3.22 \text{ (handbook)}$$

$$\log P_{\text{HCl}} = \frac{-131.35 + 2.3 \times 8.314 \times 298 \log 6^2 \times 3.22^2 - 95.36}{2.3 \times 8.314 \times 298} = -3.715$$

$$P_{\text{HCl}} = 1.93 \times 10^{-4} \text{ atm} \quad \text{or} \quad 1.93 \times 10^{-4} \times 760 = 0.147 \text{ mm Hg}$$

Problems

1. Calculate the conductance ($1/r$) of 1 *M* AgNO_3 at 291 K if the interelectrode distance is 5 cm and the area of each electrode is 2 cm^2 . The equivalent conductance of this solution is $\lambda = 94.3 \text{ mho cm}^2 \text{ g-equiv.}$

2. The molar electric conductance of 0.5 *M* K_2SO_4 at 298 K is 162.7 $\text{mho cm}^2/\text{mole}$. Determine the conductivity and equivalent conductance at this temperature.

3. During electrolysis of an AgNO_3 solution with silver electrodes the increase in the amount of salt in the anode space was 0.0625 g. What is the decrease in the amount of salt (in grams) in the cathode space?

4. A solution of silver nitrate, containing 0.18475 g AgNO_3 per 25 g of water, was subjected to electrolysis with a silver anode. After the electrolysis, the anode space contained 0.2361 g of silver nitrate per 23 g of water. Within a given period of time, 0.0780 g of silver was deposited on the electrode. Determine the transference numbers for Ag^+ and NO_3^- .

5. The absolute velocities of ions Sr^{2+} and Cl^- in a dilute solution at 291 K are 5.2×10^{-8} and $6.8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, respectively. Determine the equivalent conductances and transference numbers for the ions in the SrCl_2 solution.

6. The equivalent conductance of KClO_4 at infinite dilution and 291 K is $122.8 \text{ mho cm}^2 \text{ g-equiv}^{-1}$. The transference number for ion ClO_4^- is 0.481. Determine the mobilities of ions K^+ and ClO_4^- .

7. Calculate the equivalent conductance of 0.001 *N* LiCl and compare the result with the experimentally found value of $96.6 \text{ mho cm}^2 \text{ g-equiv}^{-1}$. The equivalent conductances of 0.001 *N* solutions of LiNO_3 , NaNO_3 , and NaCl at 291 K are, respectively, 92.9, 102.9, and $106.5 \text{ mho cm}^2 \text{ g-equiv}^{-1}$.

8. Having plotted λ versus \sqrt{c} , calculate λ_0 for KCl and compare the result with the values tabulated in the handbook. For 291 K, the following are the relationships between *c* and λ :

<i>c</i> , mole/litre	0.0001	0.0002	0.001	0.002	0.01	0.02	0.1	0.2	1
λ , $\text{mho cm}^2 \text{ g-equiv}^{-1}$	129.1	128.8	127.3	126.3	122.4	120.0	112.0	108.8	98.3

9. Define the range of concentrations for which Kohlrausch's equation is applicable (in the case of KCl solutions) if the following relations $\lambda = f(c)$ are given for 291 K:

<i>c</i> , mole/litre	0.0001	0.0002	0.001	0.002	0.01	0.02	0.1	0.2	1
λ , $\text{mho cm}^2 \text{ g-equiv}^{-1}$	129.1	128.8	127.3	126.3	122.4	120.0	112.0	108.8	98.3

10. Determine the molarity of a hydrochloric acid solution if conductometric titration of 100 ml of the HCl solution with 8 *N* NaOH has produced the following results:

V_{NaOH} , ml	0.32	0.60	0.92	1.56	2.00	2.34
$\kappa \times 10^2$, mho cm^{-1}	3.20	2.56	1.86	1.64	2.38	2.96

11. Calculate the equivalent conductance at 298 K and infinite dilution for monochloroacetic acid if the dissociation constant is $K_a = 1.55 \times 10^{-3}$ (mole/litre) and the equivalent conductance at dilution $V = 32$ litre/mole is $77.2 \text{ mho cm}^2 \text{ g-equiv}^{-1}$.

12. The equivalent conductance of $1.59 \times 10^{-4} \text{ M}$ acetic acid at 298 K is $109.78 \text{ mho cm}^2 \text{ g-equiv}^{-1}$. Calculate the dissociation constant and pH of the solution. Find the ionic mobilities in the handbook.

13. Calculate the dissociation constant of NH_4OH if at a given temperature its 0.1 *N* solution has pH 11.27. The ionic product of water at this temperature is $K_w = 0.71 \times 10^{-14}$.

14. Calculate the concentration of hydrogen ions in a solution containing 0.1 mole of acetic acid and 0.1 mole of chloroacetic acid per litre at 298 K. Find the dissociation constants of these acids in the handbook.

15. At 291 K, the conductivity κ of a saturated silver chloride solution is 1.374×10^{-6} mho cm^{-1} , and that of water, determined under the same conditions, is 4×10^{-8} mho cm^{-1} . Calculate the molar concentration of AgCl in the saturated solution. Find the ionic mobilities in the handbook.

16*. The solubility of $\text{Ba}(\text{IO}_3)_2$ at 25 °C is 8×10^{-4} mole/litre. Determine the solubility of this salt in (1) 0.1 M KNO_3 and (2) 0.03 M $\text{Ba}(\text{NO}_3)_2$. The relationship between the ionic activity coefficients and ionic strength of the solution is given in Table 5.

17*. Calculate the equivalent conductances of 5×10^{-4} and 0.1 M solutions of NaCl at 298 K, using Kohlrausch's equation. Compare the results with the tabulated values. Find the ionic mobilities at infinite dilution, the viscosity and dielectric constant of water in the handbook.

18. Calculate the activity of Na_2SO_4 , HCl, and $\text{Pb}(\text{NO}_3)_2$ in solutions with concentration $m = 1$ mole/1000 g, proceeding from the mean activity coefficients taken from the handbook.

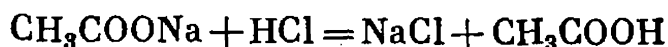
19. Calculate the ionic strength, activity coefficients of individual ions, and the mean ionic activity coefficients for solutions of electrolyte mixtures at 298 K if the solutions contain the following salts (mole/1000 g of water): MgSO_4 0.005, 0.01; LaCl_3 0.010, 0.002; and Na_2SO_4 0.020, 0.005.

20. Calculate, using the Debye-Hückel equation and the values given in Table 5, the mean ionic activity coefficient of salt BaCl_2 if $I = 2 \times 10^{-4}$ at 298 K.

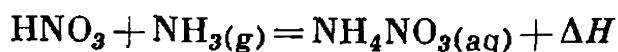
21. The ratio of partial pressures of gaseous hydrogen chloride over solutions of hydrochloric acid with $m_1 = 4$ and $m_2 = 8$ at 298 K is 0.02253. Determine the ratio of mean ionic activities a_{\pm} of these solutions. Compare the result with the values given in the handbook.

22. Given the temperature dependence of K_w (see the handbook), calculate the heat of the reaction $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$. Compare the result with the calorimetrically found heat of neutralization which is $\Delta H_{\text{neutr}} = -5.60 \times 10^3$ J/mole.

23. The heat of neutralization of acetic acid with 0.005 N NaOH at 18 °C is $-56\,105.8$ J/mole, and in the case of hydrochloric acid it equals $-57\,571.25$ J/mole. Determine the heat of the reaction

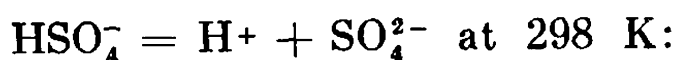


24. The heat of the reaction



proceeding in a dilute solution at 298 K is $\Delta H = -86.671$ kJ/mole. Calculate $\Delta H_f^\circ, \text{NH}_4^+$ if $\Delta H_f^\circ, \text{NH}_3(\text{g}) = -46.224$ kJ/mole.

25. Given the temperature dependence of the dissociation constant K_2 of ion HSO_4^- , calculate ΔG° , ΔH° , ΔS° , and ΔC_p° for the reaction



$$\log K_a = -\frac{475.14}{T} + 5.0435 - 0.0182T$$

or

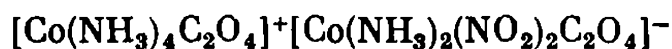
$$K_a = -\frac{318.5}{T} + 4.146 - 0.01687T$$

26. Determine the values of ΔG° , ΔH° , ΔS° , and ΔC_p° for the reaction $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$ from the relation $\log K_a = -\frac{475.14}{T} + 5.0435 - 0.0182T$ and compare the results with the standard thermodynamic values tabulated in the handbook.

27. Calculate the solubility product for $\text{Ca}(\text{OH})_2$ at 298 K, proceeding from the thermodynamic properties of individual substances and ions in aqueous solutions.

28. Calculate pH for a solution containing 0.09 mole KCl and 0.01 mole HCl per 1000 g of water. The experimental pH value is 2.078.

29. Calculate the mean ionic activity coefficients for a complex salt which is cobalt(+3) diaminedinitrooxalatecobaltate tetraaminoxalate



in aqueous solutions of sodium chloride at 15 °C:

c_{NaCl} , mole/litre	0	0.0003	0.001	0.005	0.01	0.02
Solubility of the salt, mole/litre	0.4900	0.4935	0.500	0.5220	0.5396	0.5646

30. Calculate the water solubility of silver iodide at 25 °C proceeding from the values of standard Gibbs' energies for formation of $\text{AgI}_{(\text{cr})}$, Ag^+ , and I^- from simple substances.

31. Calculate the Stokes radius of the lithium ion in an aqueous solution at infinite dilution at 298 K. Compare the result with the crystallographic radius of Li^+ , which is 0.68 Å according to Boky.

32. Given in the table is the solubility of silver iodate at 25 °C in pure water and in the presence of various amounts of potassium nitrate.

Calculate the activity coefficients of silver iodate in potassium nitrate solution of different concentrations if

$c_{\text{KNO}_3} \times 10^2$, mole/litre	0	0.1301	0.3552	0.6503	1.4100	7.0500	19.9800
Solubility of $\text{AgIO}_3 \times 10^4$, mole/litre	1.771	1.828	1.870	1.914	1.999	2.301	2.665

Plot the logarithm of the activity coefficient versus the square root of the ionic strength of the solution. Determine how well the results agree with the limiting Debye-Hückel law.

33. Calculate the pH value of $10^{-8} M$ HBr in water at 25°C , taking into account the dissociation of water into ions.

34. The temperature dependence of the ionic product of water K_w is given by the equation

$$\log K_w = -\frac{5242.39}{T} + 35.3944 - 0.00853T - 11.8261 \log T$$

Derive the equation for the temperature dependence of the heat of dissociation of water. At what temperature will the ionic product of water reach its maximum?

35. The conductivities κ of solutions of the sparingly soluble unibasic acid HA at different concentrations are $3.24 \times 10^{-4} \text{ mho cm}^{-1}$ for $8.1 \times 10^{-3} M$ HA and $6.00 \times 10^{-4} \text{ mho cm}^{-1}$ for the saturated solution. The equivalent conductances λ_0 at infinite dilution for the potassium salt KA, potassium chloride, and hydrochloric acid are 124, 150, and $426 \text{ mho cm}^{-2} \text{ g-equiv}^{-1}$, respectively. Calculate the dissociation constant and solubility of the acid.

36. Determine the solubility of silver bromide in $0.001 m$ KBr at 25°C . Find the solubility product for silver bromide in the handbook. Use the limiting Debye-Hückel law in the calculation.

37. Calculate the solubility of silver chloride in a $0.01 m$ aqueous solution of HNO_3 at 25°C . Find the solubility product for silver chloride in the handbook. Use the limiting Debye-Hückel law in the calculation. Ignore the effect of silver chloride concentration on the ionic strength of the solution.

38. Compare the tabulated value of the mean ionic activity coefficient of calcium chloride in $0.01 m$ CaCl_2 at 25°C with the results of calculations to the first and second approximations of the Debye-Hückel theory.

39. Determine the heat of the reaction $\text{H}_2\text{O}_{(\text{liq})} \rightarrow \text{H}^+ + \text{OH}^-$ (the H^+ and OH^- ions are hydrated) at 298 K, proceeding from the heats of formation of $\text{Ca}(\text{OH})_2$, CaCl_2 , and HCl , the heats of their solution, and ΔH_∞^m at infinite dilution; $\Delta H_\infty^m = -7.5 \text{ kJ}$ for $\text{Ca}(\text{OH})_2$.

40. Determine the solubility of CaCl_2 at 298 K in a $0.1 m$ aqueous solution of $\text{Ca}(\text{NO}_3)_2$. Compare the result with the solubility of CaCl_2 in pure water.

41. Determine the molar electric conductance of an aqueous solution of KCl at infinite dilution at 323 K. Use the temperature dependence of the water viscosity (see the handbook) in the calculation.

42. Determine the molar electric conductance of $0.01 M$ KCl at 323 K and $\lambda_0 = 244 \text{ mho g-equiv}^{-1} \text{ cm}^2$.

43. Proceeding from the integral heat of solution of H_2SO_4 in water at 298 K and the standard pressure of $1.0132 \times 10^5 \text{ Pa}$ at several concentrations, determine the partial molar heat of solution

of 35 m H₂SO₄ ($\Delta\bar{H}_{\text{H}_2\text{SO}_4}$). Also determine the partial molar heat of solution of water in 35 m H₂SO₄ ($\Delta\bar{H}_{\text{H}_2\text{O}}$).

44. Proceeding from the heat of evaporation of water at 298 K (see the handbook) and the partial molar heat of solution of water in 35 m H₂SO₄, determine the partial molar heat of evaporation of water from the above solution.

45. Proceeding from the saturated vapour pressure over pure water (see the handbook) and over 35 m H₂SO₄ at 298 K ($P_{\text{H}_2\text{O}} = 32.4 \text{ Pa}$), determine the activity of water at 298 K.

46. Determine the change in the chemical potential of water ($\mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2\text{O}}^\circ$) during formation of a solution of H₂O in 35 m H₂SO₄ at 298 K if the partial pressure of water vapour is 32.4 Pa and the vapour pressure over pure water is as indicated in the handbook.

Multivariant Problems

1. Proceeding from the known properties of solutions of substance A in water, (1) plot the conductivity and equivalent conductance of substance A versus dilution V , (2) check whether the aqueous solutions of substance A obey Ostwald's dilution law, and (3) given the concentration dependence of equivalent conductance, calculate the latter for substance A at infinite dilution and compare the result with the values given in the handbook:

Variant	1	2	3	4	5
Substance A	HCN	HNO ₂	HOCl	HCOOH	CH ₃ COOH
Variant	6	7	8	9	
Substance A	(CH ₃) ₂ AsOOH	C ₆ H ₅ OH	C ₆ H ₅ COOH	NH ₄ OH	

The relationship between the resistivity of the solution of substance A and concentration at 298 K is as tabulated below:

c , mole/litre	r (ohm m) for substance A								
	HCN	HNO ₂	HOCl	HCOOH	CH ₃ COOH	(CH ₃) ₂ AsOOH	C ₆ H ₅ OH	C ₆ H ₅ COOH	NH ₄ OH
0.1	3.10×10^3	4.32	927	6.06	19.6	131	7.46×10^3	9.75	2.55
0.05	4.37×10^3	5.7	1 390	8.91	27.6	180	10.80×10^3	14.1	10.3
0.03	5.84×10^3	7.5	1 810	10.3	34.8	235	14.50×10^3	18.5	14.5
0.01	10.1×10^3	13.4	3 120	18.2	61.0	402	23.50×10^3	31.4	25.8
0.005	14.3×10^3	20.4	4 560	25.9	87.0	582	32.70×10^3	48.8	100
0.003	18.3×10^3	26.8	5 560	35.8	103.0	796	41.50×10^3	57.9	143
0.001	31.9×10^3	52.7	10 000	68.5	185.0	1310	74.60×10^3	10.4	251

2. Calculate the molar electric conductance λ_m of substance A, proceeding from the equivalent conductances λ_0 , at infinite dilution for the following substances at 298 K:

Substance	$\lambda_0 \times 10^2$, mho m ² g-equiv ⁻¹	Substance	$\lambda_0 \times 10^2$, mho m ² g-equiv ⁻¹
AgCNS	1.285	La ₂ (SO ₄) ₃	1.50
Ag ₂ SO ₄	1.419	MgBr ₂	1.31
BaCl ₂	1.40	Mg(BrO ₃) ₂	1.08
CaCl ₂	1.36	MgCl ₂	1.29
LaCl ₃	1.46	Mg(CNS) ₂	1.19
La(CNS) ₃	1.36	MgF ₂	1.08
La(IO ₃) ₃	1.10	MgI ₂	1.30
MgSO ₄	1.33	SrCl ₂	1.36
PbCl ₂	1.46	TlNO ₃	1.51
PbC ₂ O ₄	1.43	Tl ₂ SO ₄	1.55
Pb(CNS) ₂	1.36		
PbSO ₄	1.10		

Variant	1	2	3	4	5	6	
Substance A	SrC ₂ O ₄	AgCl	AgIO ₃	BaSO ₄	TlBr	PbSO ₄	
Variant	7	8	9	10	11	12	
Substance A	CaC ₂ O ₄	CaF ₂	BaC ₂ O ₄	TlCl	PbF ₂	Pb(IO ₃) ₂	
Variant	13	14	15	16	17	18	19
Substance A	MgC ₂ O ₄	AgBr	AgBrO ₃	TlCNS	TlBrO ₃	TlI	TlIO ₃

3. The resistivity of a saturated solution of sparingly soluble salt A (see preceding table) at 298 K is r . The resistivity of water at the same temperature is $r_{\text{H}_2\text{O}} = 1 \times 10^4$ ohm m. Calculate (1) the solubility of salt A in pure water, (2) the solubility product of substance A*, assuming that the ionic activity coefficients are $\gamma_{\pm} = 1$ (the solutions are diluted considerably), (3) the solubility of substance A in a solution containing 0.01 mole of substance B, and (4) the solubility of substance A in a solution containing 0.01 mole of substance C. Substances A, B, and C have dissociated completely.

* The solution of the problem can be refined if the ionic strength of the solution is calculated and Table 5 or Eq. (18.22) is used to determine the activity coefficient.

The resistivity of solutions of substance A at 298 K is as follows:

Variant	$\rho \times 10^{-4}$, ohm m	Substance		
		A	B	C
1	0.0141	SrC ₂ O ₄	H ₂ C ₂ O ₄	Na ₂ SO ₄
2	0.3330	AgCl	HCl	Na ₂ SO ₄
3	0.0550	AgIO ₃	HIO ₃	Na ₂ SO ₄
4	0.3300	BaSO ₄	Na ₂ SO ₄	KBr
5	0.0038	TlBr	KBr	Na ₂ SO ₄
6	0.0248	PbSO ₄	Li ₂ SO ₄	KBr

4. Given the molality m and mean ionic activity coefficient γ_{\pm} of electrolyte A calculate the mean ionic concentration m_{\pm} , mean ionic activity a_{\pm} , and activity a .

Variant	Substance A	m , mole/1000 g	γ_{\pm}	Variant	Substance A	m , mole/1000 g	γ_{\pm}
1	CaCl ₂	1	0.500	14	Th(NO ₃) ₄	4.5	0.722
2	Ca(NO ₃) ₂	2	0.347	15	Cd(ClO ₄) ₂	5.5	41.3
3	MgI ₂	3	7.81	16	K ₃ Fe(CN) ₆	1	0.128
4	MgBr ₂	4	12.00	17	ZnI ₂	2	1.012
5	Sr(ClO ₄) ₂	5	10.09	18	Cr ₂ (SO ₄) ₃	0.3	0.0238
6	COI ₂	6	1.99	19	Th(NO ₃) ₄	0.4	0.192
7	HCl	7	4.37	20	Ba(ClO ₄) ₂	5	2.13
8	HClO ₄	8	11.83	21	Al ₂ (SO ₄) ₃	0.6	0.014
9	LiBr	9	12.92	22	K ₄ Fe(CN) ₆	0.7	0.051
10	NaOH	10	3.46	23	Na ₂ HPO ₄	0.8	0.217
11	AlCl ₃	0.5	0.331	24	K ₂ HAsO ₄	0.9	0.301
12	LaCl ₃	1.5	0.515	25	H ₂ SO ₄	10	0.559
13	SnCl ₂	3.5	1.504				

5. Calculate the chemical potential of electrolyte A in an aqueous solution at 298 K and concentration m (see the table on p.339).

6. A dilute aqueous solution of MeCl₂ is saturated with gaseous hydrogen at 298 K and 1 atm. For the reaction



Variant	Electrolyte A	m , mole/1000 g	Variant	Electrolyte A	m , mole/1000 g
1	NaOH	1	14	Al ₂ (SO ₄) ₃	0.1
2	H ₂ SO ₄	1	15	Al ₂ (SO ₄) ₃	1
3	H ₂ SO ₄	0.1	16	CsI	1
4	LiF	1	17	AlCl ₃	1
5	Ba(OH) ₂	0.1	18	AlCl ₃	0.5
6	Ba(OH) ₂	0.05	19	InSO ₄	0.1
7	NH ₄ NO ₃	1	20	Pb(NO ₃) ₂	0.1
8	UO ₂ (ClO ₄) ₂	0.1	21	H ₂ SO ₄	0.5
9	UO ₂ (ClO ₄) ₂	1	22	HNO ₃	0.5
10	CH ₃ COOCs	1	23	HNO ₃	0.1
11	Ba(NO ₃) ₂	1	24	MgSO ₄	1
12	Ca(NO ₃) ₂	0.5	25	NH ₄ Cl	1
13	HCl	0.5			

determine (1) the heat of the reaction at $P = \text{const}$, (2) the change in entropy, (3) the standard change in Gibbs' energy, (4) the logarithm of the equilibrium constant, and (5) whether the reaction will proceed spontaneously under the above conditions.

Variant	1	2	3	4	5	6
MeCl ₂	FeCl ₂	NiCl ₂	SrCl ₂	CuCl ₂	MgCl ₂	CdCl ₂

7. Given the relationship between the conductance of a weak electrolyte A and dilution at 298 K (see the handbook), plot $\lambda = f(c)$ and determine λ at $c = 6 \times 10^{-3}$ mole/litre. Calculate the degree of dissociation α of electrolyte A at a concentration of 6×10^{-3} mole/litre. Compare the result with the value calculated according to Ostwald's dilution law (find the dissociation constant of electrolyte A in the handbook). Determine the concentration of hydrogen ions in the solution of electrolyte A, the concentration of the solution being 6×10^{-3} mole/litre, as well as the pH of the solution of electrolyte A at a concentration of 6×10^{-3} mole/litre.

Variant	1	2	3	4	5	6
Electrolyte A	<i>iso</i> -C ₃ H ₇ COOH	<i>n</i> -C ₃ H ₇ COOH*	HCOOH	C ₂ H ₅ COOH	CH ₃ COOH	NH ₄ OH

* λ_{∞} , *n*-C₃H₇COOH = 32.6.

CHAPTER 19

Electromotive Force. Electrode Potentials

Basic Equations and Symbols

The emf E of a galvanic cell equals the difference between the arbitrary electrode potentials φ_1 and φ_2 of its half-cells if the diffusion potential can be ignored:

$$E = \varphi_2 - \varphi_1 \quad (19.1)$$

(subscript 2 related to the more positive electrode potential).

The electrochemical reactions occurring at electrodes and the electrodes themselves are divided into the following types.

Cation-reversible electrodes of the first kind, $\text{Me}^{n+} + ne = \text{Me}^0$, where Me^{n+} and Me^0 stand for the oxidized and reduced forms of the substance, and e stands for electron. The potential of the first-kind electrode is calculated with the aid of the Nernst equation:

$$\varphi = \varphi^\circ + \frac{RT}{nF} \ln (a_{\text{ox}}/a_{\text{red}}) \quad (19.2)$$

in which φ is the electrode potential, φ° is the standard electrode potential, n is the number of electrons involved in an elementary reaction, F is the Faraday number, and a_{red} and a_{ox} stand for the activities of the reduced and oxidized forms of the substance entering into reaction, respectively. The factor $\frac{2.3RT}{F}$ at $T = 298 \text{ K}$ and $R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}$ equals 0.059 V .

Among the electrodes of the first kind are:

(a) silver electrode

$$\text{Ag}^+ | \text{Ag}, \quad \text{Ag}^+ + e = \text{Ag}^0, \quad n = 1, \quad a_{\text{ox}} = a_{\text{Ag}^+}, \quad a_{\text{red}} = a_{\text{Ag}} = 1$$

$$\varphi = \varphi_{\text{Ag}^+, \text{Ag}}^\circ + \frac{0.059}{1} \log a_{\text{Ag}^+} \quad (19.3)$$

(b) amalgam electrode

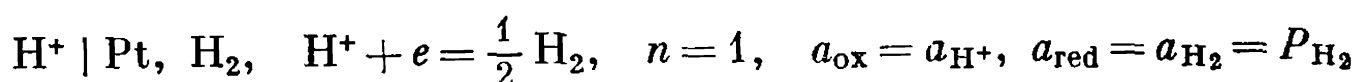
$$\text{Cd}^{2+} | [\text{Cd}] (\text{Hg}) \quad \text{Cd}^{2+} + 2e = [\text{Cd}]_{\text{am}}, \quad n = 2, \quad a_{\text{ox}} = a_{\text{Cd}^{2+}}$$

$$a_{\text{red}} = a_{[\text{Cd}]_{\text{am}}} = \frac{P_{\text{Cd}}}{P_{\text{Cd}}^\circ}$$

$$\varphi = \varphi_{\text{Cd}^{2+}, [\text{Cd}] (\text{Hg})}^\circ + \frac{0.059}{2} \log \frac{a_{\text{Cd}^{2+}}}{a_{[\text{Cd}]}} \quad (19.4)$$

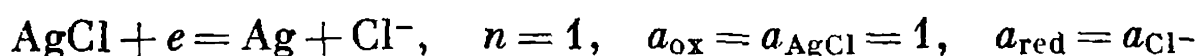
where $\varphi_{\text{Cd}^{2+}, [\text{Cd}] (\text{Hg})}^\circ$ is the potential of the amalgam electrode with the cadmium activity in the amalgam being $a_{[\text{Cd}]} = 1$;

(c) gas electrode



$$\varphi = \varphi_{\text{H}^+, \text{H}_2}^\circ + \frac{0.059}{1} \log \frac{a_{\text{H}^+}}{P_{\text{H}_2}^{1/2}} \quad (19.5)$$

A *second-kind (anion-reversible) electrode* is essentially a metal coated with a sparingly soluble salt of the same metal and is at equilibrium with the solution containing the corresponding anion:

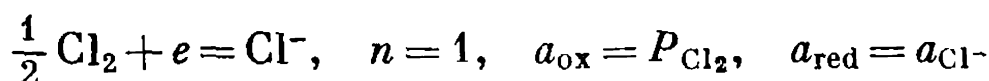


$$\varphi = \varphi_2^\circ - \frac{0.059}{1} \log a_{\text{Cl}^-} \quad (19.6)$$

$$\varphi_2^\circ = \varphi_{\text{Ag}^+, \text{Ag}}^\circ + 0.059 \text{SP}_{\text{AgCl}} \quad (19.7)$$

where $\varphi_{\text{Ag}^+, \text{Ag}}^\circ$ is the standard potential of the cation-reversible silver electrode, and $\text{SP}_{\text{AgCl}} = a_{\text{Ag}} a_{\text{Cl}^-}$ is the solubility product of silver chloride. The second-kind electrodes include:

(a) gas electrode



$$\varphi = \varphi_{\text{Cl}_2, \text{Cl}^-}^\circ - \frac{0.059}{1} \log (a_{\text{Cl}^-} / P_{\text{Cl}_2}^{1/2}) \quad (19.8)$$

(b) calomel electrode $\text{Cl}^- | \text{Hg}_2\text{Cl}_2, \text{Hg}$ which provides the site for the electrode reaction $\text{Hg}_2\text{Cl}_2 + 2e = \text{Hg} + 2\text{Cl}^-$:

$$\varphi_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2, \text{H}} = \varphi_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2, \text{H}}^\circ - \frac{0.059}{2} \log a_{\text{Cl}^-}$$

(c) silver-chloride electrode $\text{Cl}^- | \text{AgCl}, \text{Ag}$ which provides the site for the electrode reaction $\text{AgCl} + e = \text{Ag} + \text{Cl}^-$:

$$\varphi_{\text{Cl}^-/\text{AgCl}, \text{Ag}} = \varphi_{\text{Cl}^-/\text{AgCl}, \text{Ag}}^\circ - \frac{0.059}{1} \log a_{\text{Cl}^-}$$

Redox electrodes. A redox electrode is essentially an inert metal immersed into a solution containing the oxidized and reduced forms. The Nernst equation takes the following form for such electrodes:

$$\varphi_{\text{red, ox}} = \varphi_{\text{red, ox}}^\circ + \frac{0.059}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}} \quad (19.9)$$

where a_{ox} (a_{o}) is the activity of the oxidized ion, and a_{red} (a_{R}) is the activity of the reduced ion;

(a) simple electrodes:

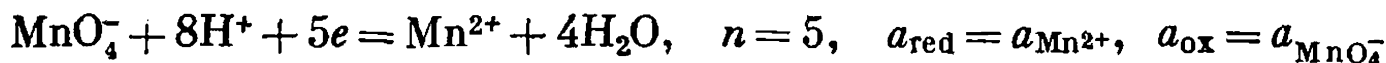


$$\varphi = \varphi_{\text{Fe}^{3+}, \text{Fe}^{2+}}^{\circ} + \frac{0.059}{1} \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \quad (19.10)$$



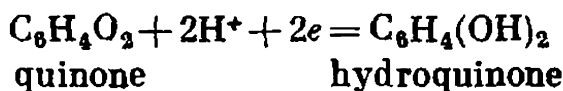
$$\varphi = \varphi_{\text{MnO}_4^-, \text{MnO}_4^{2-}}^{\circ} + \frac{0.059}{1} \log (a_{\text{MnO}_4^-} / a_{\text{MnO}_4^{2-}}) \quad (19.11)$$

(b) composite electrodes:



$$\varphi = \varphi_{\text{Mn}^{2+}/\text{MnO}_4^-}^{\circ} + \frac{0.059}{5} \log \frac{a_{\text{MnO}_4^-}}{a_{\text{Mn}^{2+}}} \quad (19.12)$$

Quinhydrone electrode:



$$n = 2, \quad a_{\text{red}} = a_{\text{hq}} = 1, \quad a_{\text{ox}} = a_{\text{q}} = 1$$

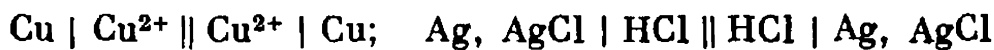
$$\varphi = \varphi_{\text{q}, \text{hq}}^{\circ} + \frac{0.059}{2} \log a_{\text{H}^+}^2 + \varphi_{\text{q}, \text{hq}}^{\circ} - 0.059\text{pH} \quad (19.13)$$

The relationship between the equilibrium constant of a chemical reaction and the standard electrode potentials is written as

$$\log K = \frac{(\varphi_2^{\circ} - \varphi_1^{\circ})n}{0.0592} \quad (T = 298 \text{ K}) \quad (19.14)$$

where $\varphi_2^{\circ} > \varphi_1^{\circ}$.

In the case of concentration cells, the Nernst equation (in the absence of the diffusion potential) for electrodes of the following type:



$$\begin{matrix} a_1 & a_2 \\ a_2 > a_1 \end{matrix}$$

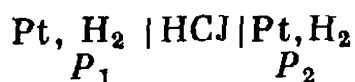
$$\begin{matrix} a_1 & a_2 \\ a_2 > a_1 \end{matrix}$$

takes the form

$$E = \frac{0.059}{n} \log (a_2/a_1) \quad (19.15)$$

where a_1 and a_2 stand for the activities of ions Cu^{2+} and Cl^- , respectively.

For second-kind electrodes of the following type:

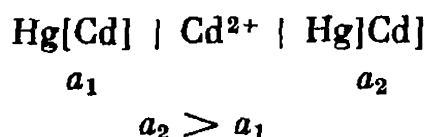


Eq. (19.15) takes the form

$$E = \frac{0.059}{2} \log (P_1/P_2) \quad (19.16)$$

where P_1 and P_2 are hydrogen pressures; $P_1 > P_2$.

For an amalgam electrode of the following type:

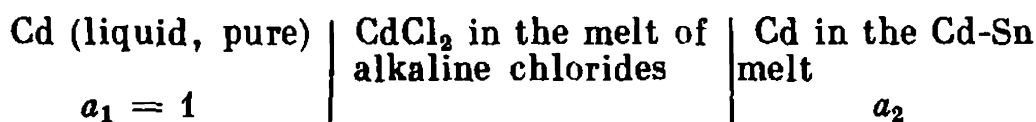


the Nernst equation will be

$$E = \frac{0.059}{2} \log (a_2/a_1) \quad (19.17)$$

where a_1 and a_2 are the activities of metallic cadmium in the amalgam.

For a cell of the following type:

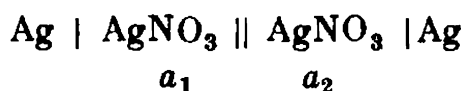


Equation (19.17) becomes

$$E = \frac{0.059}{2} \log a_2 \quad (19.18)$$

where a_2 is the activity of cadmium in the Cd-Sn melt.

To calculate the emf of a concentration cell in the case where the diffusion potential cannot be ignored:



where a_1 and a_2 stand for the activities of silver ions, $a_2 > a_1$, the following equation is used:

$$E = \frac{2\lambda_{0, \text{NO}_3^-}}{\lambda_{0, \text{Ag}^+} + \lambda_{0, \text{NO}_3^-}} 0.059 \log (a_2/a_1) \quad (19.19)$$

in which $\lambda_{0, \text{NO}_3^-}$ and λ_{0, Ag^+} are the mobilities of the anion and the cation.

The thermodynamic functions ΔG , ΔS , and ΔH for electrochemical reactions are calculated using the following equations:

$$\Delta G = -nEF \quad (19.20)$$

$$\Delta S = nF \left(\frac{dE}{dT} \right)_P \quad (19.21)$$

$$\Delta H = -nFE + nTF \left(\frac{dE}{dT} \right)_P \quad (19.22)$$

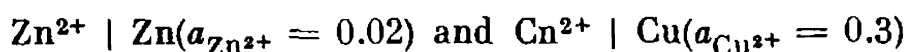
$$\Delta C_P = nFT \frac{d^2E}{dT^2} \quad (19.23)$$

$$E = -\frac{\Delta H}{nF} + T \left(\frac{dE}{dT} \right)_P \quad (19.24)$$

in which n is the number of electrons involved in the reaction, F is the Faraday number, and E is the emf.

Exercises

1. Given the standard electrode potentials of copper and zinc, calculate the emf of a cell consisting of two half-cells:



Solution. To calculate the emf use the equations

$$E = \varphi_2 - \varphi_1$$

$$\varphi_i = \varphi_i^\circ + \frac{RT}{nF} \log (a_{\text{ox}}/a_{\text{red}})$$

$$\frac{2.3RT}{F} = \frac{2.3 \times 8.314 \times 298}{96487} = 0.059 \text{ V}$$

Find the standard electrode potentials in the handbook $\varphi_{\text{Cu}^{2+}, \text{Cu}}^\circ = 0.337 \text{ V}$ and $\varphi_{\text{Zn}^{2+}, \text{Zn}}^\circ = -0.763 \text{ V}$. Since the copper half-cell is more electropositive, then

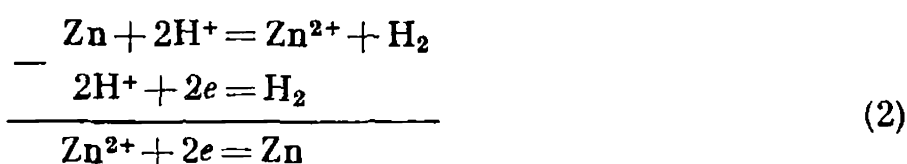
$$E = \varphi_{\text{Cu}^{2+}, \text{Cu}}^\circ - \varphi_{\text{Zn}^{2+}, \text{Zn}}^\circ + \frac{0.059}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Zn}^{2+}}}, \quad E = 1.135 \text{ V}$$

2. Determine the direction of the reaction $\text{Zn} + 2\text{HCl}_{(\text{sol})} = \text{H}_2 + \text{ZnCl}_{2(\text{sol})}$, proceeding from the standard electrode potentials, and write the circuit of the corresponding electrochemical cell.

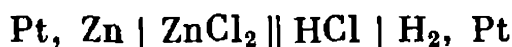
Solution. Write the equation of one of the probable electrode reactions:



and subtract it from the overall equation written in the ionic form:



Find the standard electrode potentials for electrode reactions (1) and (2) in the handbook; $\varphi_1^\circ = 0$, $\varphi_2^\circ = -0.763$ V. Since $\varphi_1^\circ > \varphi_2^\circ$, according to Eq. (19.1), subtract (2) from (1). The result will be $2\text{H}^+ + \text{Zn} = \text{H}_2 + \text{Zn}^{2+}$. Write the circuit of the cell according to the electrode potential values:

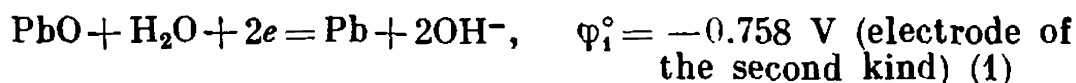


3. Proceeding from the galvanic cell circuit



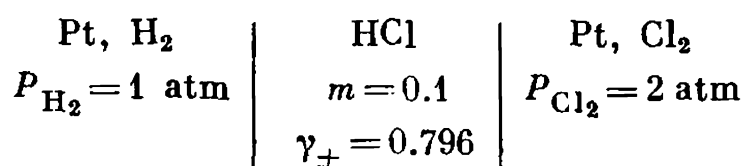
write the equation of the corresponding reaction.

Solution. As can be inferred from the above circuit, the potentials φ of the electrodes making up the cell are determined by the following substances: (1) Pb, PbO, OH^- and (2) H_2 , OH^- . Find the corresponding electrode reactions and standard potentials in the handbook:



Since $\varphi_1^\circ > \varphi_2^\circ$, subtract (2) from (1), and the result will be $\text{PbO} + \text{H}_2 = \text{Pb} + \text{H}_2\text{O}$.

4. Given the gas cell circuit



calculate the potential of the chlorine electrode ($\varphi_{\text{Cl}_2, \text{Cl}^-}^\circ$) and the emf of the cell as a whole at 298 K.

Solution. To calculate the potential $\varphi_{\text{Cl}_2, \text{Cl}^-}$ use Eq. (19.8):

$$\varphi_{\text{Cl}_2, \text{Cl}^-} = \varphi_{\text{Cl}_2, \text{Cl}^-}^\circ - 0.059 \left(\log a_{\text{Cl}^-} - \frac{1}{2} \log P_{\text{Cl}_2} \right)$$

$$\varphi_{\text{Cl}_2, \text{Cl}^-}^\circ = 1.358 \text{ V (handbook)}$$

$$\varphi_{\text{Cl}_2, \text{Cl}^-} = 1.358 - 0.059 \left(\log 0.1 \times 0.796 - \frac{1}{2} \log 2 \right) = 1.440 \text{ V}$$

Calculate the emf of the cell using Eq. (19.1). To do this determine the potential of the hydrogen cell according to Eq. (19.5):

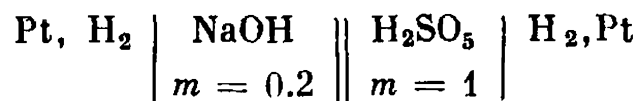
$$\varphi_{\text{H}^+, \text{H}_2} = \varphi_{\text{H}^+, \text{H}_2}^\circ + 0.059 \left(\log a_{\text{H}^+} + \frac{1}{2} \log P_{\text{H}_2} \right)$$

$$\varphi_{\text{H}^+, \text{H}_2}^\circ = 0, \quad \varphi_{\text{H}^+, \text{H}_2} = 0.059 (\log 0.1 \times 0.796) = -0.065 \text{ V}$$

Substitution of the obtained values into Eq. (19.1) gives

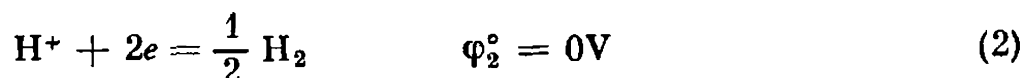
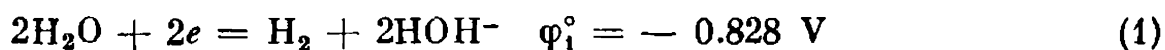
$$E = 1.440 - (-0.065) = 1.505 \text{ V}$$

5. Given the galvanic cell circuit



$T = 298 \text{ K}$, $P_{\text{H}_2} = 1 \text{ atm}$ calculate the emf of the cell.

Solution. Use Eq. (19.1) for the calculation. Write the equations of the electrode reactions and find the corresponding standard potentials φ^0 and mean ionic activity coefficients γ_{\pm} in the handbook:



Use the mean activity coefficients and concentrations of ions to calculate their activities:

$$a_{\text{OH}^-} = a_{\pm} = m\gamma_{\pm} = 0.1 \times 0.766 = 0.0766, \quad a_{\text{H}_2\text{O}} = 1$$

for the NaOH solution, $m = 0.1$ and $\gamma_{\pm} = 0.766$; for the H_2SO_4 solution, $m = 1$ and $\gamma_{\pm} = 0.132$;

$$a_{\text{H}^+} \cong a_{\pm} = \sqrt[3]{4} m\gamma_{\pm}, \quad a_{\pm} = \sqrt[3]{4} \times 1 \times 0.132 = 0.21$$

Calculate the electrode potentials φ_2 and φ_1 using Eqs. (19.5) and (19.2):

$$\varphi_2 = \varphi_{\text{H}^+, \text{H}_2}^0 + \frac{0.059}{1} \left(\log a_{\text{H}^+} - \frac{1}{2} \log P_{\text{H}_2} \right)$$

$$\varphi_{\text{H}^+, \text{H}_2}^0 = 0, \quad \varphi_2 = 0.059 (\log 0.21) = -0.04 \text{ V}$$

$$\varphi_1 = \varphi_{\text{H}_2\text{O}, \text{H}_2, \text{OH}^-}^0 = \varphi_{\text{H}_2\text{O}, \text{H}_2, \text{OH}^-}^0 - \frac{0.059}{1} \left(\log a_{\text{OH}^-} - \frac{1}{2} \log P_{\text{H}_2} \right)$$

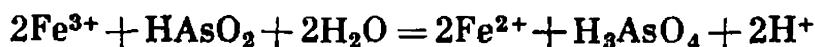
$$\varphi_{\text{H}_2\text{O}, \text{H}_2, \text{OH}^-}^0 = -0.828 \text{ V (handbook)}$$

$$\varphi_1 = -0.828 - 0.059 \log 0.0766 = -0.762 \text{ V}$$

Substitution of the obtained values of φ_1 and φ_2 into Eq. (19.1) gives

$$E = -0.04 + 0.762 = 0.758 \text{ V}$$

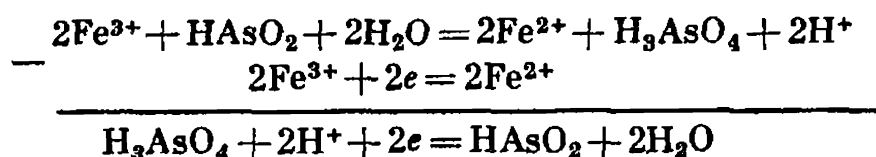
6. Calculate the emf and write the circuit of a galvanic cell in which the following reaction proceeds reversibly:



at 1 atm and 298 K. The activities of the ions involved in the reaction are $a_{\text{Fe}^{2+}} = 0.005$, $a_{\text{Fe}^{3+}} = 0.02$, $a_{\text{H}_3\text{AsO}_2} = 0.2$, $a_{\text{HAsO}_2} = 0.1$, $a_{\text{H}^+} = 0.01$, and $a_{\text{H}_2\text{O}} = 1$.

Solution. Derive the equations for the electrode reactions. To this end, subtract the equation of one of the probable electrode reactions

from that given above:



Find the corresponding standard electrode potentials in the handbook:
 $\varphi_1^\circ = \varphi_{\text{H}_3\text{AsO}_4, 2\text{H}^+, \text{HAsO}_2}^\circ = 0.560 \text{ V}$ and $\varphi_2^\circ = \varphi_{\text{Fe}^{3+}, \text{Fe}^{2+}}^\circ = 0.771 \text{ V}$.

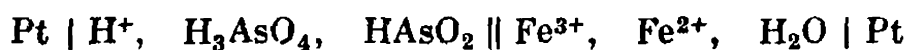
Calculate the electrode potentials using Eq. (19.2):

$$\varphi_1 = \varphi_{\text{H}_3\text{AsO}_4, 2\text{H}^+, \text{HAsO}_2}^\circ + \frac{0.059}{n} \log \frac{a_{\text{H}_3\text{AsO}_4} a_{\text{H}^+}^2}{a_{\text{HAsO}_2} a_{\text{H}_2\text{O}}^2}, \quad n = 2$$

$$\varphi_1 = 0.560 + \frac{0.059}{2} \log \frac{0.2 \times 0.01^2}{0.1} = 0.451 \text{ V}$$

$$\varphi_2 = \varphi_{\text{Fe}^{3+}, \text{Fe}^{2+}}^\circ + \frac{0.059}{2} \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} = 0.771 + \frac{0.059}{2} \log \frac{0.02}{0.005} = 0.789 \text{ V}$$

Substitution of the obtained values of φ_1 and φ_2 into Eq. (19.1) gives $E = 0.789 - 0.451 = 0.338 \text{ V}$. The circuit of the cell is



7. Given the galvanic cell circuit



The emf of the cell at 298 K is $E = 0.610 \text{ V}$. Calculate the normal potential $\varphi_{\text{Tl}^+, [\text{Tl}]\text{Hg}}^\circ$ of the amalgam electrode.

Solution. According to Eq. (19.1), $\varphi_2 = 0.281 \text{ V}$ for the calomel electrode (the handbook). Then,

$$\varphi_1 = \varphi_{\text{Tl}^+, [\text{Tl}]\text{Hg}}^\circ + 0.059 \log \frac{a_{\text{Tl}^+}}{a_{[\text{Tl}]}}$$

$$a_{\text{Tl}^+} = m\gamma_{\pm} = 0.1 \times 0.73 = 0.073$$

Substitute the obtained values into Eq. (19.1):

$$0.61 = 0.281 - \varphi_{\text{Tl}^+, [\text{Tl}]\text{Hg}}^\circ - 0.059 \log \frac{0.073}{0.0628}$$

and calculate

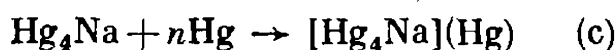
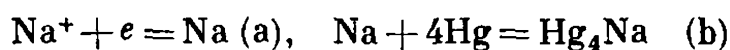
$$\varphi_{\text{Tl}^+, [\text{Tl}]\text{Hg}}^\circ = 0.281 - 0.61 - 0.059 \log \frac{0.073}{0.0628} = -0.333 \text{ V}$$

8. The normal potential of the sodium amalgam electrode at 298 K is $\varphi_{\text{Na}^+, [\text{Na}]\text{Hg}}^\circ = -1.86 \text{ V}$. The normal potential of a sodium electrode is $\varphi_{\text{Na}^+, \text{Na}}^\circ = -2.714 \text{ V}$. Explain this wide difference between the two values.

Solution. Denote the potential difference

$$\varphi_{\text{Na}^+, [\text{Na}]\text{Hg}}^\circ - \varphi_{\text{Na}^+, \text{Na}}^\circ = -0.85 \text{ V} \quad (1)$$

by E^s . Use the state diagram of the Hg-Na system, which indicates that dilute (liquid) sodium amalgams are essentially solutions of the intermetallic compound Hg_4Na in mercury. Consequently, the equation of the corresponding electrode reaction will be $\text{Na}^+ + e = [\text{Hg}_4\text{Na}] (\text{Hg})$. Substitute this reaction by the following processes:



Since the change in Gibbs' energy is dependent only on the initial and final states of the system, rather than the path of the process, then

$$\Delta G_{\text{reac}} = \Delta G_{(\text{a})} + \Delta G_{(\text{b})} + \Delta G_{(\text{c})} \quad (2)$$

Division of Eq. (1) by nF gives

$$\varphi_{\text{Na}^+, [\text{Na}](\text{Hg})}^\circ = \varphi_{\text{Na}^+, \text{Na}}^\circ + \varphi_2^\circ + \varphi_3^\circ \quad (3)$$

Comparison of Eqs. (1) and (3) gives

$$E^s = \varphi_2^\circ + \varphi_3^\circ$$

where E^s is a measure of chemical interaction between the metal and mercury.

9. The standard potential of the electrode $\text{OH}^- | \text{H}_2, \text{Pt}$ ($P_{\text{H}_2} = 1 \text{ atm}$) is $\varphi_1^\circ = -0.828 \text{ V}$. Proceeding from this value, calculate the ionic product of water K_w at 298 K if the Nernst equation takes the form

$$\varphi_1 = \varphi_1^\circ - 0.059 \log a_{\text{OH}^-} \quad (1)$$

Solution. Any aqueous solution contains hydrogen ions, and the Nernst equation for the hydrogen electrode is

$$\varphi_1 = \varphi_{\text{H}^+, \text{H}_2}^\circ + 0.059 \log a_{\text{H}^+} \quad (2)$$

However, since the circuit of the above electrode indicates that the emf is dependent on the concentration of ions OH^- , express a_{H^+} in terms of a_{OH^-} and the ionic product of water K_w :

$$a_{\text{H}^+} = K_w / a_{\text{OH}^-} \quad (3)$$

Then, combining Eqs. (2) and (3) gives

$$\varphi_1 = \varphi_{\text{H}^+, \text{H}_2}^\circ + 0.059 \log K_w - 0.059 \log a_{\text{OH}^-} \quad (4)$$

Comparison of Eqs. (1) and (4) suggests that

$$\varphi_1^\circ = \varphi_{\text{H}^+, \text{H}_2}^\circ + 0.059 \log K_w = -0.825 \text{ V}$$

Since $\varphi_{\text{H}^+, \text{H}_2}^\circ = 0$,

$$\log K_w = -\frac{0.825}{0.0592} = -14.014, \quad K_w = 1.03 \times 10^{-14}$$

10. The standard potential of the electrode $\text{Cl}^-|\text{CuCl}$ is $\varphi_2^\circ = 0.137$ V. Calculate the solubility product SP_{CuCl} at 298 K.

Solution. According to the equation

$$\varphi_2^\circ = \varphi_1^\circ + 0.059 \log \text{SP}$$

in which φ_1° is the normal potential of the cation-reversible copper electrode $\text{Cu}^+|\text{Cu}$, $\varphi_1^\circ = 0.521$ V, we have

$$\log \text{SP} = \frac{0.137 - 0.521}{0.059} = -6.486, \quad \text{SP} = 3.19 \times 10^{-7} \text{ (mole/litre)}^2$$

11. Calculate the equilibrium constant of the reaction $\text{Cd}^{2+} + \text{Zn} = \text{Zn}^{2+} + \text{Cd}$, if $\varphi_{\text{Cd}^{2+}, \text{Cd}}^\circ = -0.403$ V and $\varphi_{\text{Zn}^{2+}, \text{Zn}}^\circ = -0.763$ V.

Solution. Calculate the equilibrium constant using Eq. (19.14)

$$\log K = \frac{(-0.403 - (-0.763)) \times 2}{0.0592} = 12.16$$

$$K = 1.45 \times 10^{12}$$

12. Calculate the equilibrium constant for the reaction $\text{Cd}^{2+} + \text{Zn} = \text{Zn}^{2+} + \text{Cd}$ proceeding from the standard thermodynamic quantities for the ions, given in the handbook.

Solution. Calculate the equilibrium constant of the reaction using the equations

$$\log K = -\Delta G_{\text{reac}}^\circ / 2.3RT \quad \text{and} \quad \Delta G_{\text{reac}}^\circ = \Delta G_{\text{Zn}^{2+}}^\circ - \Delta G_{\text{Cd}^{2+}}^\circ$$

Find the values of ΔG° for ions Zn^{2+} and Cd^{2+} in the handbook:

$$\Delta G_{\text{Zn}^{2+}}^\circ = -147.30 \text{ kJ/mole}, \quad \Delta G_{\text{Cd}^{2+}}^\circ = -77.794 \text{ kJ/mole}$$

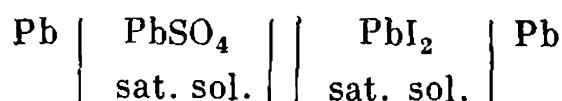
Then,

$$\Delta G_{\text{reac}}^\circ = -147.30 - (-77.794) = -69.504 \text{ kJ/mole}$$

Consequently,

$$\log K = \frac{69\,504}{2.3 \times 8.314 \times 298} = 12.17$$

13. Calculate the emf of the cell



at 298 K, proceeding from the solubility products for PbSO_4 and PbI_2 (see the handbook).

Solution. Calculate the emf using the equation

$$E = \frac{0.059}{2} \log \frac{(a_{\text{Pb}^{2+}})_2}{(a_{\text{Pb}^{2+}})_1}$$

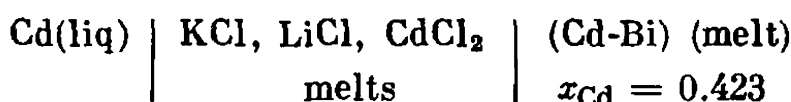
Determine the mean ionic activities from the solubility products:

$$\text{SP } (a_{\pm})_2 = \sqrt[3]{\text{SP}_{\text{PbI}_2}}, \quad (a_{\pm})_1 = \sqrt{\text{SP}_{\text{PbSO}_4}}$$

$$\text{SP}_{\text{PbI}_2} = 8 \times 10^{-9} \text{ (mole/litre)}^3, \quad \text{SP}_{\text{PbSO}_4} = 1.6 \times 10^{-8} \text{ (mole/litre)}^2$$

$$E = \frac{0.059}{2} \log \frac{\sqrt[3]{8 \times 10^{-9}}}{\sqrt{1.6 \times 10^{-8}}} = 0.019 \text{ V}$$

14. Given the cell circuit



$T = 773 \text{ K}$, and the cell emf $E = 0.0329 \text{ V}$, calculate the activity a_{Cd} , activity coefficient γ_{Cd} , and partial pressure of cadmium P_{Cd} . The saturated pure cadmium pressure is $P_{\text{Cd}}^0 = 14.84 \text{ mm Hg}$.

Solution. The cell is of the concentration type. To find the activity of cadmium in the Cd-Bi melt use the equation

$$E = - \frac{2.3 \times 8.314 \times 773}{2 \times 96487} \log a_{\text{Cd}}$$

$$\log a_{\text{Cd}} = - \frac{0.0329 \times 2 \times 96487}{2.3 \times 8.314 \times 773} = -0.430$$

$$\log a_{\text{Cd}} = \bar{1}.57, \quad a_{\text{Cd}} = 0.372$$

To calculate the activity coefficient of cadmium in the melt, use the equation

$$\gamma_{\text{Cd}} = a_{\text{Cd}}/x_{\text{Cd}} = 0.372/0.423 = 0.879$$

Calculate the partial pressure of cadmium using the equation

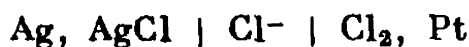
$$P_{\text{Cd}} = a_{\text{Cd}} P_{\text{Cd}}^0$$

$$P_{\text{Cd}} = 14.84 \times 0.372 = 5.22 \text{ mm Hg } (7.36 \times 10^2 \text{ Pa})$$

15. Calculate the useful work W' of the reaction $\text{Ag} + 0.5\text{Cl}_2 = \text{AgCl}$, proceeding from the standard electrode potentials, if $P_{\text{Cl}_2} = 1 \text{ atm}$ and $T = 298 \text{ K}$.

Solution. The useful work of the reaction at P and $T = \text{const}$ will be $W = -\Delta G$. For an electrochemical reaction, $\Delta G^\circ = -nE^\circ F$. The emf of the cell is $E^\circ = \varphi_2^\circ - \varphi_1^\circ$, where φ_2° and φ_1° stand for the standard potentials of the electrodes making up the cell. The above

reaction proceeds in the following cell:



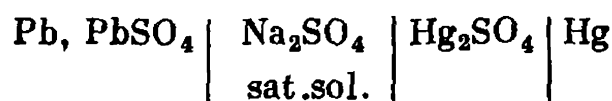
$$a_{\text{Cl}^-} = 1 \quad P_{\text{Cl}_2} = 1$$

$$\varphi_2^\circ = \varphi_{\text{Cl}_2, \text{Cl}^-}^\circ = 1.360 \text{ V}, \quad \varphi_1^\circ = \varphi_{\text{AgCl, Ag, Cl}^-}^\circ = 0.220 \text{ V}$$

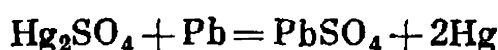
$$E^\circ = 1.360 - 0.220 = 1.14 \text{ V and } W' = nE^\circ F$$

$$= 1.14 \times 96\,487 = 109.99 \text{ kJ/mole}$$

16. Given the cell circuit



and the overall reaction in the electrochemical system



calculate the emf at 298 K and the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_P$ proceeding from the tabulated standard thermodynamic quantities.

Solution. Use the following equations for the calculation:

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P$$

$$\Delta S = \sum S_f - \sum S_r$$

$$E = -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_P$$

$$\Delta H^\circ = \sum \Delta H_{f, f}^\circ - \sum \Delta H_{f, r}^\circ$$

Find the entropies and heats of formation for the reactants in the handbook:

Substance	Hg(lq)	PbSO ₄	Hg ₂ SO ₄	Pb
$S^\circ, \text{J mole}^{-1} \text{K}^{-1}$	76.1	148.67	100.83	64.85
$\Delta H^\circ, \text{kJ/mole}$	0	-918.1	-742.0	0

The entropy of the reaction,

$$\Delta S^\circ = 2S_{\text{Hg}}^\circ + S_{\text{PbSO}_4}^\circ - S_{\text{Hg}_2\text{SO}_4}^\circ - S_{\text{Pb}}^\circ$$

will be

$$\Delta S^\circ = 35.19 \text{ J mole}^{-1} \text{K}^{-1}$$

The temperature coefficient of emf will be

$$\left(\frac{\partial E}{\partial T} \right)_P = \frac{35.19}{2 \times 96\,487} = 1.85 \times 10^{-4} \text{ V/K}$$

The heat of the electrochemical reaction is

$$\Delta H^\circ = \Delta H_{f, \text{PbSO}_4}^\circ - \Delta H_{f, \text{Hg}_2\text{SO}_4}^\circ = -918.1 - (-742.0)$$

$$= -176.11 \text{ kJ/mole}$$

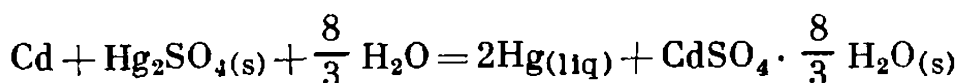
Then, the emf of the galvanic cell will be

$$E = -\frac{(-176.1 \times 10^3)}{2 \times 96487} + 298 \times 1.85 \times 10^{-4} = 0.968 \text{ V}$$

17. Given the temperature dependence of the emf of a Weston cell:

$$E = 1.018 - 0.041 \times 10^{-3} (t - 20) - 9.5 \times 10^{-7} (t - 20)^2 + 10^{-8} (t - 20)^3$$

for the reaction

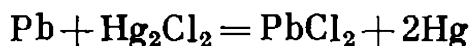


calculate ΔC_P° at 298 K.

Solution. Calculate $\left(\frac{\partial^2 E}{\partial T^2}\right)_P$ by resorting to double differentiation of the equation $E = f(T)$. For 298 K, $(\partial^2 E / \partial T^2)_P = -16 \times 10^{-7} \text{ V/K}$. According to Eq. (19.23),

$$\Delta C_P^\circ = -16 \times 10^{-7} \times 2 \times 9.65 \times 10^4 \times 298 = 92.1 \text{ J/mole}$$

18. The temperature coefficient of a cell whose operation is based on the reaction



is $\left(\frac{\partial E}{\partial T}\right)_P = 1.45 \times 10^{-4} \text{ V/K}$. Determine the amount of heat released (absorbed) during operation of the cell and compare the result with the heat of the reaction at 298 K.

Solution. According to the equation $Q = nFT \left(\frac{\partial E}{\partial T}\right)_P$ the heat of the reversible process is $Q = 2 \times 96487 \times 298 \times 1.45 \times 10^{-4} = 8.338 \text{ kJ/mole}$.

The heat of the irreversible process equals that of the chemical reaction

$$\Delta H_{\text{reac}}^\circ = \Delta H_{f, \text{PbCl}_2}^\circ - \Delta H_{f, \text{Hg}_2\text{Cl}_2}^\circ$$

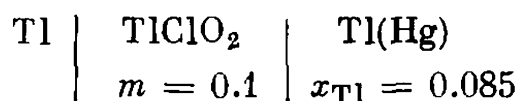
$$\Delta H_{f, \text{PbCl}_2}^\circ = -359.1 \text{ kJ/mole}, \quad \Delta H_{f, \text{Hg}_2\text{Cl}_2}^\circ = -264.85 \text{ kJ/mole}$$

$$\Delta H_{\text{reac}}^\circ = -94.25 \text{ kJ/mole}$$

Comparison of the heats of the reversible and irreversible processes gives $8.338 \times 100 / 94.25 = 8.85\%$.

Thus, the heat released during operation of the cell is 8.85% of the total decrease in enthalpy.

19. Given the circuit of the concentration cell



and its emf which is 0.071 V at 298 K as well as its temperature coefficient which is $(\partial E/\partial T)_P = 1.8 \times 10^{-4}$ V/K, calculate the relative molar enthalpy ΔH_{Tl}^m of dissolution of thallium in the amalgam if $x_{Tl} = 0.085$.

Solution. Calculate ΔH_{Tl}^m using the equation

$$\Delta H_{Tl}^m = 96\,487 \left(T \left(\frac{\partial E}{\partial T} \right)_P - E \right) = 96\,487 (298 \times 1.8 \times 10^{-4} - 0.071) = -1686 \text{ J/mole}$$

20. Calculate the partial molar heat of dilution of HCl (ΔH_{HCl}) from the concentration $m_1 = 0.1$ to that in a finitely dilute solution (m_2). Base your calculation on the temperature dependence of the mean ionic activity coefficient of hydrochloric acid.

For a solution with $m = 0.1$,

$T, \text{ K}$	293.16	303.16
γ_{\pm}	0.7985	0.7940

Solution. Use the equations

$$\log \frac{a_{HCl}(T_2)}{a_{HCl}(T_1)} = \frac{\Delta \bar{H}_{HCl} (T_2 - T_1)}{2.3RT_2T_1}, \quad a_{HCl} = \gamma_{\pm}^2 m^2$$

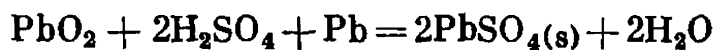
$$\log \left(\frac{\gamma_{\pm}(T_2)}{\gamma_{\pm}(T_1)} \right)^2 = \frac{\Delta \bar{H}_{HCl}}{2.3R} \left(\frac{T_2 - T_1}{T_2T_1} \right)$$

Substitution of the numerical values gives

$$\log \left(\frac{0.794}{0.7985} \right)^2 = \frac{\Delta \bar{H}_{HCl}}{2.3 \times 8.314} \left(\frac{10}{293.15 \times 303.15} \right)$$

$$\Delta \bar{H}_{HCl} = 8.314 - 832.62 \text{ J/mole}$$

21. Calculate the emf of a lead battery at 298 K, in which the sulphuric acid content by weight is 21.4% and $m_{H_2SO_4} = 2.78$ moles/1000 g. The cell reaction is



Gibbs' energies of formation of the substances participating in the reaction are as follows: ΔG_f° (kJ/mole): $H_2O_{(l)}$ 234.40, $PbSO_4$ 814.38, PbO_2 218, $H_2SO_{4(lnf.dil.)}$ 746.15.

The mean ionic activity coefficient of sulphuric acid is $\gamma_{\pm} = 0.138$, and the water vapour pressure over the solution is 21.35 mm Hg.

Solution. To calculate the emf use the equation $E = -\Delta G/nF$. But first calculate ΔG using the equation

$$\Delta G = 2\Delta G_{f, H_2O}^\circ + 2\Delta G_{f, PbSO_4}^\circ - \Delta G_{f, PbO_2}^\circ - 2\Delta \bar{G}_{f, H_2SO_4}$$

Find $\Delta\bar{G}_{\text{H}_2\text{O}}$ and $\Delta\bar{G}_{\text{H}_2\text{SO}_4}$ with the aid of the equations

$$\Delta\bar{G}_{\text{H}_2\text{O}} = \Delta G^\circ_{\text{H}_2\text{O}} + RT \ln a_{\text{H}_2\text{O}}$$

$$a_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P^\circ_{\text{H}_2\text{O}}} = \frac{21.35}{23.76} = 0.897$$

$$\Delta\bar{G}_{\text{H}_2\text{O}} = -234.40 + 8.314 \times 298 \ln 0.897 = -237.67 \text{ kJ/mole}$$

When calculating $\Delta\bar{G}_{\text{H}_2\text{SO}_4(\text{sol})}$, the standard condition is assumed to involve a finitely dilute solution ($m = 1$). Then, according to the handbook,

$$a_{\text{H}_2\text{SO}_4} = 4(m\gamma_\pm)^3, \quad a_{\text{H}_2\text{SO}_4} = 4(2.78 \times 0.138)^3 = 0.226$$

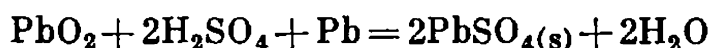
$$\begin{aligned} \Delta\bar{G}_{\text{H}_2\text{SO}_4} &= \Delta G^\circ_{\text{H}_2\text{SO}_4(\text{inf.dil.})} + RT \ln 4(m\gamma_\pm)^3 \\ &= -746.15 + 8.314 \times 298 \ln 4(0.138 \times 2.78)^3 = -749.84 \text{ kJ/mole} \end{aligned}$$

Then, $\Delta G = 2(-237.67) + 2(-814.38) + 218 + 2 \times 749.84 = -386.24 \text{ kJ/mole}$. Calculate E :

$$E = -\frac{-386\,240}{2 \times 96\,487} = 2.002 \text{ V}$$

22. Calculate the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_P$ for a lead battery if it contains 21.4% (wt) H_2SO_4 and $m_{\text{H}_2\text{SO}_4} = 2.78$ moles/1000 g.

The cell reaction is



The entropies of the substances participating in the reaction are as follows, S° (J mole⁻¹ K⁻¹): $\text{H}_2\text{O}_{(\text{liq})}$ 69.96, PbSO_4 148.67, PbO_2 71.92, Pb 64.80, $\text{H}_2\text{SO}_{4(\text{inf.dil.})}$ 18 ± 1 .

The partial molar heat of solution of water is $\Delta H^\text{m}_{\text{H}_2\text{O}} = 196.65 \text{ J/mole}$. The partial molar heat of dilution of sulphuric acid is $\Delta\bar{H}_{\text{H}_2\text{SO}_4} = -2824.5 \text{ J/mole}$. The mean ionic activity coefficient of H_2SO_4 is $\gamma_\pm = 0.138$, and the water vapour pressure over the solution is $P_{\text{H}_2\text{O}} = 21.35 \text{ mm Hg}$.

Solution. Calculate $\left(\frac{\partial E}{\partial T}\right)_P$ using the equation

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{n96\,487}, \text{ where } n = 2$$

Calculate ΔS using the equation

$$\Delta S = 2S^\circ_{\text{PbSO}_4} + 2\bar{S}_{\text{H}_2\text{O}} - S^\circ_{\text{PbO}_2} - S^\circ_{\text{Pb}} - 2\bar{S}_{\text{H}_2\text{SO}_4}$$

According to the equations

$$\bar{S}_{\text{H}_2\text{O}} = S^\circ_{\text{H}_2\text{O}} + \frac{\Delta H^\text{m}_{\text{H}_2\text{O}}}{T} - R \ln a_{\text{H}_2\text{O}}$$

and

$$\bar{S}_{\text{H}_2\text{SO}_4} = S_{\text{H}_2\text{SO}_4(\text{sol})}^\circ - \frac{\Delta H_{\text{H}_2\text{SO}_4}}{298} - R \ln a_{\text{H}_2\text{SO}_4}$$

$$\begin{aligned}\bar{S}_{\text{H}_2\text{O}} &= 69.96 + \frac{196.65}{298} - 8.314 \times 2.3 \log 0.897 \\ &= 72.27 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\bar{S}_{\text{H}_2\text{SO}_4} &= 18 + \frac{2824.5}{298} - 8.314 \times 2.3 \log 4 (0.138 \times 2.78)^3 \\ &= 80.87 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

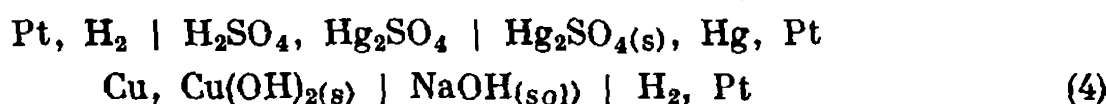
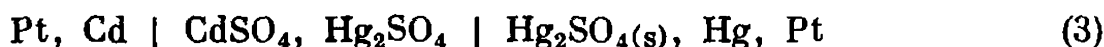
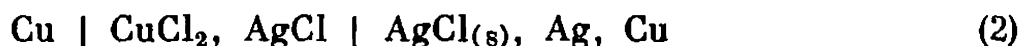
Then,

$$\begin{aligned}\Delta S &= 2 \times 148.69 + 2 \times 72.27 - 71.92 - 64.80 - 2 \times 80.87 \\ &= 143.42 \text{ J mole}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\left(\frac{\partial E}{\partial T} \right)_P = \frac{143.42}{2 \times 96487} = 7.4 \times 10^{-4} \text{ V/K}$$

Problems

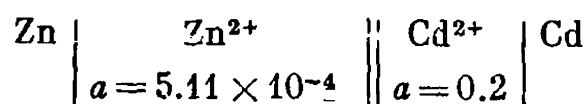
1. Write the equations of the reactions occurring in the following cells:



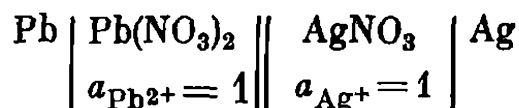
2. Write the circuits of the cells and half-cells which are the sites of the following reactions:



3. Calculate the emf of the cell

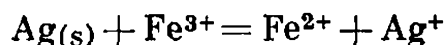


4. Write the equation of the reaction for the cell



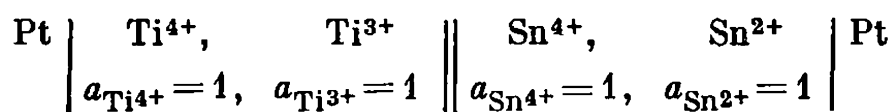
Calculate the emf. Find the necessary data in the handbook.

5. Proceeding from the standard electrode potentials, determine whether the reaction



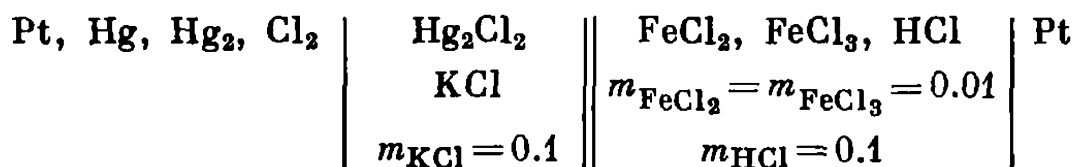
in an aqueous solution is possible at 298 K. Calculate the equilibrium constant of the reaction.

6. Calculate the emf of the cell



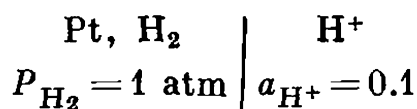
Write the cell reaction and determine whether it is spontaneous or not if $\varphi_{\text{Ti}^{4+}, \text{Ti}^{3+}}^\circ = 0.04 \text{ V}$ and $\varphi_{\text{Sn}^{4+}, \text{Sn}^{2+}}^\circ = 0.15 \text{ V}$.

7. A cell consists of a normal calomel electrode and a ferric-ferrous one:

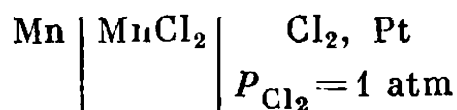


The emf of this cell at 298 K is 0.446 V. (Hydrochloric acid is added to prevent hydrolysis.) Assuming that the activity coefficients of ions Fe^{2+} and Fe^{3+} are 0.75 and 0.87, respectively, calculate the value of φ° for the ferric-ferrous electrode containing 0.1 M HCl.

8. Determine the electrode potential for

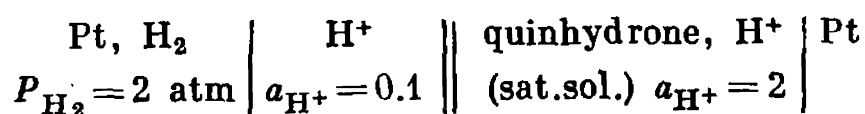


9. Proceeding from the standard electrode potentials (handbook) for the cell

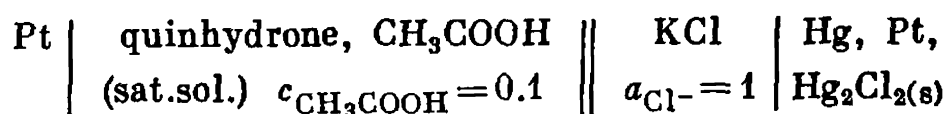


calculate the emf of the cell and determine (a) which of the half-cells is electronegative, (b) whether the sign of the emf of the half-cells can be changed by varying the ion concentration or gas pressure, and (c) the characteristics of the half-cells the direction of the emf of which depends on the solution concentration and the pressure of the gas saturating the electrode.

10. Determine the emf of the cells



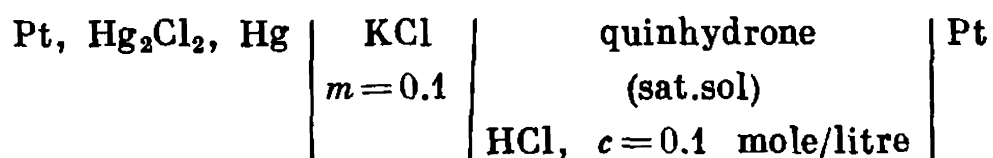
and



at 298 K.

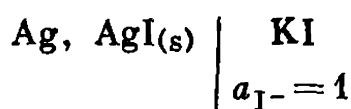
The standard electrode potential of the quinhydrone half-cell is 0.6994 V. The dissociation constant of acetic acid is $K = 1.75 \times 10^{-5}$.

Determine the pH value for hydrochloric acid if for the cell



$E = 0.301 \text{ V}$ at 298 K.

11. Calculate the standard electrode potential of the half-cell



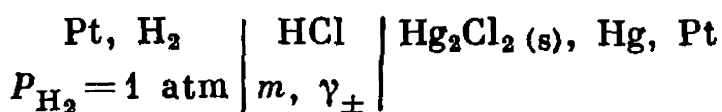
proceeding from the solubility product for AgI (handbook) and the standard electrode potential of Ag, Ag⁺.

12. Given the emf of the cell



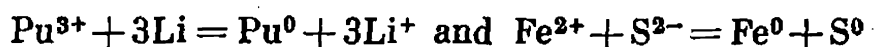
at 298 K, determine the activity of cadmium iodide in the solution ($E = 0.286 \text{ V}$).

13. The standard emf of the cell



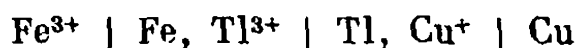
at 298 K is 0.2680 V. Calculate the emf for the following conditions: $P_{\text{H}_2} = 0.01$ and 0.1 atm, $m = 1$ and 10^{-3} mole/1000 g, and $\gamma_{\pm} = 0.809$ and 0.966, respectively.

14. Proceeding from the standard electrode potentials, calculate the equilibrium constants of the reactions



at 298 K.

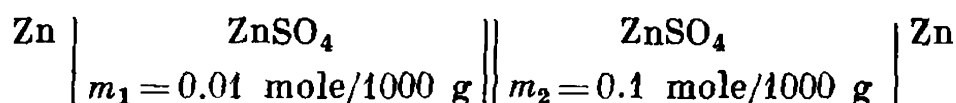
15. Calculate the standard electrode potentials of the half-cells



at 298 K, proceeding from the standard electrode potentials for the electrodes $\text{Fe}^{2+} \mid \text{Fe}$, $\text{Fe}^{3+} \mid \text{Fe}^{2+}$, $\text{Tl}^{3+} \mid \text{Tl}^+$, $\text{Tl}^+ \mid \text{Tl}$, and $\text{Cu}^{2+} \mid \text{Cu}$ (handbook) and the equilibrium constant of the reaction $\text{Cu} + \text{Cu}^{2+} = 2\text{Cu}^+$:

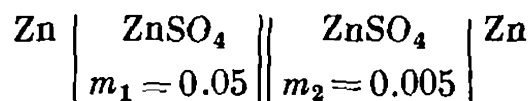
$$K_a = a_{\text{Cu}^+}^2 / a_{\text{Cu}^{2+}} = 6.31 \times 10^{-7}$$

16. The emf of the cell



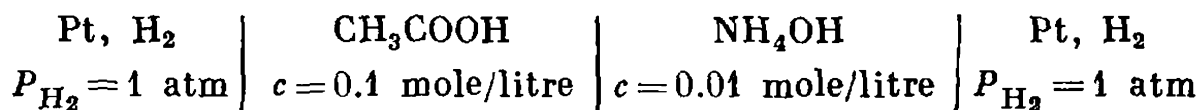
is 0.0235 V at 298 K. Can the diffusion potential be ignored in this case? (Compare the calculated emf with the one given above and draw an appropriate conclusion.)

17. The emf of the cell



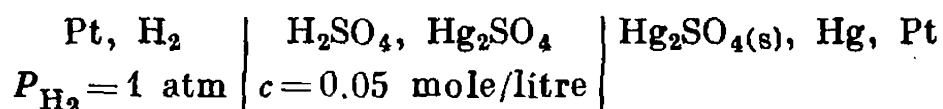
is 0.0185 V at 298 K. Calculate γ_{\pm} for the concentrated solution if for the dilute solution $\gamma_{\pm} = 0.477$.

18. Calculate the emf of the cell



at 298 K. Find the dissociation constants of acetic acid and ammonium hydroxide in the handbook.

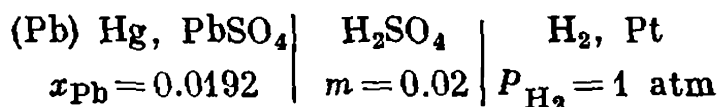
19. Determine the activity coefficient for 1 M H_2SO_4 if for 0.05 M H_2SO_4 the mean ionic activity coefficient is 0.34, the density of a 1 M solution is 1.060 g/cm³, and the emf of the cell



is 0.7546 V for 0.05 M H_2SO_4 and 0.6744 V for 1 M H_2SO_4 .

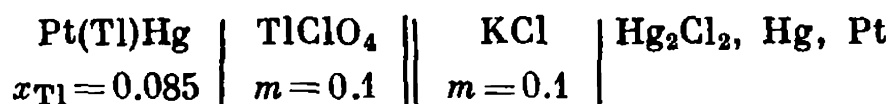
20. A cell is composed of zinc amalgams of different concentrations. Calculate the emf assuming that $a_{\text{Zn}} = c_{\text{Zn}}$. Determine the direction of migration of the Zn^{2+} ions in the solution if, at 298 K, $c_1 = 0.00337$ mole/litre and $c_2 = 0.00011$ mole/litre.

21. The emf of the cell



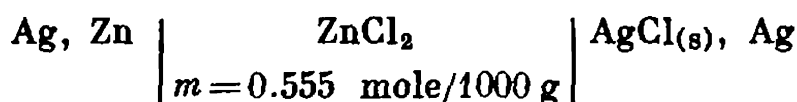
is 0.1238 V at 298 K. The standard potential of the amalgam electrode is $\Phi_{(\text{Pb})\text{Hg}, \text{PbSO}_4, \text{SO}_4^{2-}} = -0.353$ V. Calculate the activity of lead in the amalgam and its activity coefficient.

22. The emf of the cell



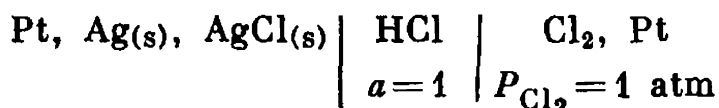
is 0.61 V at 298 K. The activity of thallium in the amalgam is $a_{\text{Tl}} = 0.0628$. Calculate the standard potential of the amalgam electrode.

23. Proceeding from the standard electrode potentials, write for the cell



the equation of the reaction and calculate the change ΔH in enthalpy at 273 K, the amount Q of heat released if the cell reaction is reversible, and φ° of the cell if $E = 1.125$ V and $(\partial E / \partial T)_P = -0.0004$ V/K at 273 K.

24. The emf of the cell



as a function of temperature is given by the equation

$$E = 0.977 + 5.7 \times 10^{-4} (350 - t) - 1.48 \times 10^{-7} (350 - t)^2$$

Calculate ΔC_p° and compare the result with the value given in the handbook.

25. Write the equation of the reaction occurring in the cell

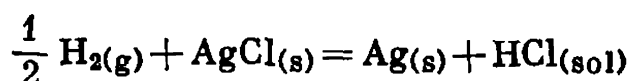


Proceeding from

$T, \text{ K}$	293	298	303
emf, V	0.0663	0.0684	0.0705

and the standard thermodynamic quantities given in the handbook, calculate the heat of the reaction in the reversible and irreversible cases.

26. In a cell which is the site of the reaction



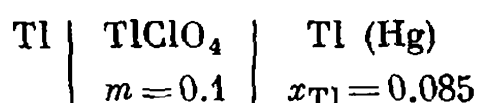
the emf depends on temperature as follows:

$T, \text{ K}$	273	283	293	298	303	313	323	333
$E, \text{ V}$	0.236	0.231	0.225	0.222	0.219	0.212	0.204	0.196

Write the circuit of the cell and calculate $(\partial E/\partial T)_P$, ΔG° , ΔH° , ΔS° , ΔA , ΔU° , W , and Q of the reversible reaction at 298 K by the graphical differentiation method. Tabulate the results and check them with the aid of the equation

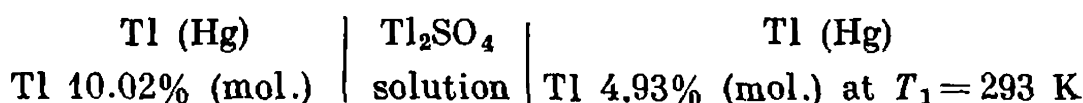
$$E = 0.2224 - 645 \times 10^{-6} (T - 298) - 3.284 \times 10^{-6} (T - 298)^2$$

27. The emf of the concentration cell



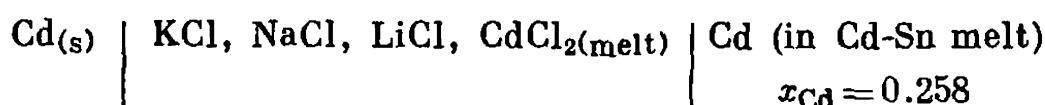
is 0.071 V at 298 K. The temperature coefficient of the cell is $\left(\frac{\partial E}{\partial T}\right)_P = 1.8 \times 10^{-4} \text{ V/K}$. Calculate $a_{[\text{Tl}]}$, $\gamma_{[\text{Tl}]}$, ΔG_{Tl}^m , and ΔS_{Tl}^m for the thallium dissolved in mercury and determine the departure of the Tl-Hg solution from Raoult's law.

28. The emf of the concentration cell



is $E_1 = 0.02948 \text{ V}$ at $T_1 = 293 \text{ K}$ and $E_2 = 0.02997 \text{ V}$ at $T_2 = 303 \text{ K}$. Calculate the differential heat of dilution of thallium, $\Delta \bar{H}_{\text{Tl}}$, at 293 K.

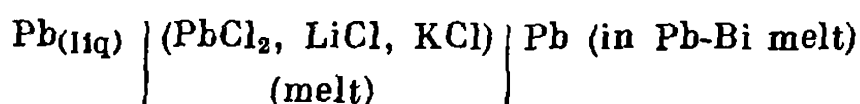
29. The emf of the cell



is 0.0324 V at 756 K, $P_{\text{Cd}}^\circ = 9.2 \text{ mm Hg}$. Determine (a) the activity of cadmium in the melt, (b) the cadmium vapour pressure over the melt, and (c) the departures from Raoult's law.

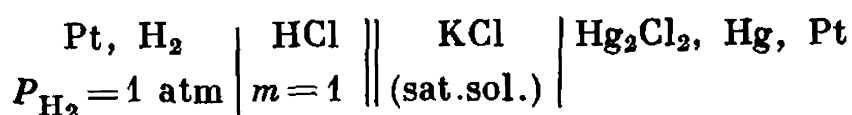
30. One electrode of an electrolytic cell is liquid thallium, and the other electrode is an alloy of thallium with lead. The electrolyte is a mixture of molten salts LiCl, KCl, and TlCl. When the molar fraction of thallium in the alloy reaches 0.20, the emf of the cell is 0.115 V at 711 K. Calculate the activity, activity coefficient, and vapour pressure for the alloy. The saturated pure thallium vapour pressure is $P_{\text{Tl}}^\circ = 5 \times 10^{-5} \text{ mm Hg}$.

31. In the case of the cell



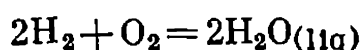
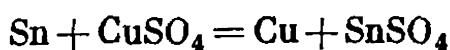
$x_{\text{Pb}} = 0.23$, $E = 59.76 \times 10^{-3}$ V, $dE/dT = 64.4 \times 10^{-6}$ V/K, and $P_{\text{Pb}}^{\circ} = 5.1 \times 10^{-5}$ atm at 700 K. Calculate the activity, activity coefficient, and vapour pressure over the melt for lead, as well as ΔG_{Pb}^m , ΔH_{Pb}^m , and ΔS_{Pb}^m .

32. Calculate the emf of the cell



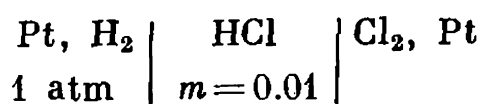
at 298 K with due account for the diffusion potential. Find the necessary data in the handbook and in the appended table.

33. Calculate the equilibrium constants for the following reactions:



at 298 K, proceeding from the standard electrode potentials.

34. The emf of the cell



at 298 K depends on pressure:

P , atm	1	50	100
E , V	1.5962	1.6419	1.6451

Determine the fugacity of Cl_2 and the fugacity coefficient at 50 and 100 atm.

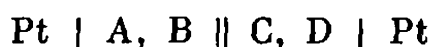
35. In a fuel cell, the chemical reaction $\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O}_{(\text{liq})}$ occurs. What is the maximum value of the empirical energy to be obtained per mole of H_2 and what is the maximum emf?

Multivariant Problems

1. Calculate the emf of a concentration cell consisting of metal A in electrolyte B in concentrations m_1 and m_2 mole/1000 g at 298 K. Determine the activity from the mean activity coefficient given in the handbook or (for dilute solutions) from the ionic strength. Calculate the emf of a cell made up of a hydrogen electrode in the solution of electrolyte C with concentration m_3 mole/1000 g and a calomel half-cell in which the concentration of KCl is m_4 mole/1000 g, and determine the pH of the solution containing electrolyte C. Do not take the diffusion emf into account. At 298 K, the standard potential of the calomel electrode ($a_{\text{Cl}^-} = 1$) is 0.268 V, and the ionic product of water is 1.008×10^{-14} . Find the dissociation constants of weak electrolytes in the handbook.

Variant	Substance		m_1	m_2	C	m_3	m_4	P_{H_2} , atm
	A	B						
1	Co	Co(NO ₃) ₂	0.1	0.7	NH ₄ OH	0.5	0.35	0.50
2	Co	Co(NO ₃) ₂	0.02	0.7	NH ₄ OH	1.0	0.4	1.00
3	Ni	NiSO ₄	0.1	0.7	HCOOH	0.3	0.03	0.50
4	Ni	NiSO ₄	1.5	0.2	NH ₄ OH	1.0	0.3	0.50
5	Cu	CuCl ₂	1.0	2.0	HCl	0.01	0.1	0.20
6	Cu	CuCl ₂	0.2	0.05	HCl	3.0	0.5	2.00
7	Cu	CuCl ₂	2.0	0.06	NaOH	2.0	1.0	2.00
8	Cu	CuCl ₂	0.02	0.6	NaOH	8.0	1.5	2.00
9	Cu	CuSO ₄	0.1	0.5	HBr	0.95	4.0	0.20
10	Cu	CuSO ₄	0.01	1.0	HBr	1.0	0.45	0.20
11	Zn	ZnCl ₂	0.005	1.0	C ₆ H ₅ OH	0.9	0.2	0.50
12	Zn	ZnCl ₂	0.5	0.01	C ₆ H ₅ OH	0.1	0.25	1.00
13	Zn	ZnCl ₂	0.5	0.02	H ₂ O	—	3.0	1.00
14	Zn	ZnCl ₂	1.0	3.0	H ₂ O	—	3.5	1.00
15	Zn	ZnSO ₄	0.01	0.1	C ₆ H ₅ OH	0.3	1.0	0.50
16	Zn	ZnSO ₄	3.0	0.002	C ₆ H ₅ OH	0.7	1.5	0.50
17	Ag	AgNO ₃	0.1	1.0	CH ₃ COOH	0.1	4.0	0.10
18	Ag	AgNO ₃	0.2	2.0	CH ₃ COOH	1.0	0.2	0.10
19	Ag	AgNO ₃	0.1	3.0	CH ₃ COOH	0.3	0.3	2.00
20	Ag	AgNO ₃	1.0	0.5	HCOOH	0.1	0.7	2.00
21	Cd	Cd(NO ₃) ₂	0.2	0.6	NaOH	1.4	2.0	3.00
22	Cd	Cd(NO ₃) ₂	2.0	0.7	NaOH	0.1	2.5	3.00
23	Cd	CdSO ₄	0.005	2.0	H ₂ SO ₄	0.5	3.0	3.00
24	Cd	CdSO ₄	1.0	0.2	H ₂ SO ₄	17.0	3.5	0.10
25	Pb	Pb(NO ₃) ₂	0.002	0.02	HCOOH	1.0	2.5	2.00

2. Write the redox reaction and calculate its equilibrium constant for the redox cell



proceeding from the standard electrode potentials of the half-cells. Determine whether the direction of the reaction can be changed practically by varying the component concentrations. Assume that $a_{H_2O} = 1$ and $a_{H^+} = 0.2$. (see the table on p. 363).

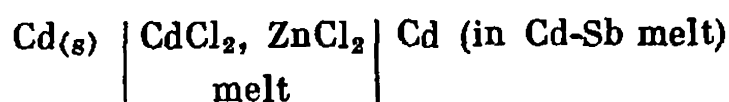
3. The temperature dependence of emf is given for a reversible cell reaction. At a given temperature T calculate the emf E , the change in Gibbs' energy, ΔG , the change in enthalpy, ΔH , the change in entropy, ΔS , the change in Helmholtz' energy, ΔA , and the heat Q released or absorbed in the course of the process. Base your calculations on one mole of reactant (see the table on p. 364).

Vari- ant	A	B	C	D	a_A	a_B	a_C	a_D
1*	$(\text{MnO}_4)^-$	Mn^{2+}	Cr^{3+}	Cr^{2+}	0.1	0.02	0.01	0.01
2*	$(\text{MnO}_4)^-$	Mn^{2+}	H_3AsO_4	HAsO_2	0.005	0.015	0.001	0.03
3*	$(\text{MnO}_4)^-$	$(\text{MnO}_4)^{2-}$	$(\text{MnO}_4)^-$	Mn^{2+}	0.009	0.014	0.001	0.07
4*	$(\text{MnO}_4)^-$	Mn^{2+}	Sn^{4+}	Sn^{2+}	0.02	0.01	0.08	0.15
5	$(\text{MnO}_4)^-$	$(\text{MnO}_4)^{2-}$	V^{3+}	V^{2+}	0.018	0.005	0.1	0.15
6	Fe^{3+}	Fe^{2+}	Cr^{3+}	Cr^{2+}	0.005	0.15	0.1	0.001
7	$\text{Fe}(\text{CN})_6^{3-}$	$\text{Fe}(\text{CN})_6^{4-}$	Co^{3+}	Co^{2+}	0.06	0.06	0.04	0.005
8	Cr^{3+}	Cr^{2+}	Tl^{3+}	Tl^{2+}	0.006	0.1	0.08	0.002
9	Co^{3+}	Co^{2+}	$\text{Fe}(\text{CN})_6^{3-}$	$\text{Fe}(\text{CN})_6^{4-}$	0.04	0.009	0.06	0.001
10*	Co^{3+}	Co^{2+}	$(\text{MnO}_4)^-$	Mn^{2+}	0.1	0.006	0.01	0.007
11	Co^{3+}	Co^{2+}	Cr^{3+}	Cr^{2+}	0.012	0.01	0.005	0.06
12*	Cu^{2+}	Cu^+	UO_2^{2+}	U^{4+}	0.007	0.016	0.002	0.05
13	Cu^{2+}	Cu^+	Sn^{4+}	Sn^{2+}	0.14	0.009	0.002	0.08
14*	H_3AsO_4	HAsO_2	$(\text{MnO}_4)^-$	$(\text{MnO}_4)^{2-}$	0.08	0.04	0.02	0.007
15*	H_3AsO_4	HAsO_2	V^{3+}	V^{2+}	0.15	0.005	0.005	0.01
16	V^{3+}	V^{2+}	Tl^{3+}	Tl^+	0.016	0.007	0.001	0.1
17*	Sn^{4+}	Sn^{2+}	H_3AsO_4	HAsO_2	0.06	0.008	0.04	0.003
18	Sn^{4+}	Sn^{2+}	Pu^{4+}	Pu^{3+}	0.08	0.06	0.007	0.005
19	Sn^{4+}	Sn^{2+}	Tl^{3+}	Tl^+	0.1	0.05	0.02	0.01
20	Ce^{4+}	Ce^{3+}	Co^{3+}	Co^{2+}	0.08	0.007	0.02	0.005
21	Ce^{4+}	Ce^{3+}	$(\text{MnO}_4)^-$	$(\text{MnO}_4)^{2-}$	0.01	0.02	0.01	0.04
22	Tl^{3+}	Tl^+	Ce^{4+}	Ce^{3+}	0.009	0.04	0.02	0.02
23*	UO_2^{2+}	U^{4+}	Fe^{3+}	Fe^{2+}	0.012	0.1	0.01	0.1
24*	UO_2^{2+}	U^{4+}	Fe^{3+}	Fe^{2+}	0.04	0.08	0.06	0.003
25*	Pu^{4+}	Pu^{3+}	$(\text{UO}_2)^{2+}$	U^{4+}	0.02	0.1	0.08	0.001

* The reaction involves H^+ and H_2O .

Vari- ant	T, K	Variant	T, K	Reaction	Equation $E = f(T)$
1	273	2	323	$C_6H_4O_2 + 2H^+ = C_6H_4(OH)_2 + 2e$	$E = 0.6990 - 7.4 \times 10^{-4}(T - 298)$
3	343	4	363	$Zn + 2AgCl = ZnCl_2 + 2Ag$	$E = 1.125 - 4.02 \times 10^{-4}T$
5	278	6	343	$Zn + Hg_2SO_4 = ZnSO_4 + 2Hg$	$E = 1.4328 - 1.19 \times 10^{-3}(T - 298)$
7	273	8	298	$Ag + Cl^- = AgCl + e$	$E = 0.2224 - 6.4 \times 10^{-4}(T - 298)$
9	273	10	363	$Cd + Hg_2SO_4 = CdSO_4 + 2Hg$	$E = 1.0183 - 4.06 \times 10^{-5}(T - 293)$
11	303	12	273	$Cd + 2AgCl = CdCl_2 + 2Ag$	$E = 0.869 - 6.5 \times 10^{-4}T$
13	293	14	323	$Cd + PbCl_2 = CdCl_2 + Pb$	$E = 0.331 - 4.8 \times 10^{-4}T$
15	273	16	363	$2Hg + ZnCl_2 = Hg_2Cl_2 + Zn$	$E = 1 + 9.4 \times 10^{-5}(T - 288)$
17	273	18	353	$2Hg + SO_4^{2-} = Hg_2SO_4 + 2e$	$E = 0.6151 - 8.02 \times 10^{-4}(T - 298)$
19	333	20	353	$Pb + 2AgI = PbI_2 + 2Ag$	$E = 0.259 - 1.38 \times 10^{-4}T$
21	273	22	298	$2Hg + 2Cl^- = Hg_2Cl_2 + 2e$	$E = 0.2438 - 6.5 \times 10^{-4}(T - 298)$
23	363			$2Ag + Hg_2Cl_2 = 2AgCl + 2Hg$	$E = 0.556 + 3.388 \times 10^{-4}T$
24	353			$Hg_2Cl_2 + 2KOH = Hg_2O + 2KCl + H_2O$	$E = -0.0947 + 8.37 \times 10^{-4}T$
25	298			$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$	$E = 0.5353 + 1.45 \times 10^{-4}T$

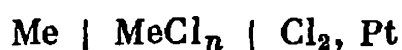
4. Given the emf of the cell



at 753 K for different concentrations of cadmium in the melt, calculate the activity and activity coefficient of Cd and the pressure of its vapour over the melt. The pure cadmium vapour pressure is $P^\circ = 9.01$ mm Hg.

Variant			x_{Cd}	$E \times 10^3, \text{ V}$	Variant			x_{Cd}	$E \times 10^3, \text{ V}$
1	11	21	0.796	3.31	6	16	0.559	33.85	
2	12	22	0.818	7.20	7	17	0.434	52.00	
3	13	23	0.750	11.56	8	18	0.401	56.51	
4	14	24	0.676	18.96	9	19	0.375	59.90	
5	15	25	0.588	29.69	10	20	0.344	63.95	

5. Calculate the emf of the cell



at temperature T , using the standard thermochemical quantities from the handbook.

Variant	Me	MeCl_n	$T, \text{ K}$	Variant	Me	MeCl_n	$T, \text{ K}$
1	Ag	AgCl	700	9	Mg	MgCl_2	900
2	Cd	CdCl_2	800	10	Na	NaCl	1000
3	Ca	CaCl_2	1000	11	Pb	PbCl_2	700
4	Co	CoCl_2	1000	12	Sn	SnCl_2	500
5	Cs	CsCl	900	13	Cr	CrCl_3	1400
6	Ba	BaCl_2	1200	14	Tl	TlCl	700
7	K	KCl	1000	15	La	LaCl_3	1100
8	Li	LiCl	800				

CHAPTER 20

Adsorption

Basic Equations and Symbols

The adsorption of a gas at $T = \text{const}$ is given by Langmuir's adsorption isotherm equation

$$\Gamma = \Gamma_{\infty} \frac{kP}{1 + kP} \quad (20.1)$$

in which Γ is the amount of gas adsorbed by 1 g of the adsorbent or 1 cm² of its surface, Γ_{∞} is the maximum amount of gas that can be adsorbed by 1 g of the adsorbent (or 1 cm² of its surface) at a given temperature, k is the adsorption equilibrium constant, and P is the equilibrium gas pressure. Equation (20.1) expressed in terms of degree of filling θ takes the form

$$\theta = kP/(1 + kP) \quad (20.2)$$

The degree of filling is determined from the following ratio:

$$\theta = \Gamma/\Gamma_{\infty} \quad (20.3)$$

Langmuir's adsorption isotherm can be expressed as the adsorbed gas volume:

$$V = V_m kP/(1 + kP) \quad (20.4)$$

The constants in Langmuir's equation are calculated using the relation

$$\frac{P}{\Gamma} = \frac{1}{k\Gamma_{\infty}} + \frac{1}{\Gamma_{\infty}} P \quad (20.5)$$

or

$$\frac{1}{V} = \frac{1}{V_m} + \frac{k}{V_m P} \quad (20.6)$$

where V is the volume of the adsorbed gas, and V_m is that of the adsorbed gas covering completely the surface of 1 g of the adsorbent, both volumes being reduced to normal conditions.

The area S of the surface of 1 g of the adsorbent is

$$S = \frac{V_m N_A}{22.414} s \quad (20.7)$$

where s is the area occupied by one molecule of the adsorbate on the surface of the adsorbent.

Adsorption from solution is given by Langmuir's equation of the following type:

$$\Gamma = \Gamma_{\infty} kc/(1 + kc) \quad (20.8)$$

where c is the equilibrium concentration of the adsorbate in the solution.

A more rigorous adsorption equation is

$$P = \frac{\theta}{k(1-\theta)(1+k\theta)} \quad (20.9)$$

where k is a constant taking into account the forces of attraction between adsorbate molecules.

To determine the mean degree of filling of the adsorbent surface use is made of Freundlich's isotherm equation

$$x/m = kc^n \quad (20.10)$$

or

$$\log(x/m) = \log k + n \log c \quad (20.11)$$

in which x is the amount of the adsorbate, m is the weight of the adsorbent, and k and n are constants.

Assuming that adsorption involves several layers, Brunauer, Emmett, and Teller have derived the following adsorption isotherm equation (BET equation):

$$\frac{P}{V(P_s - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_s} \quad (20.12)$$

in which V is the total volume of the adsorbed gas, V_m is the adsorbed gas volume in the case where the entire surface of the adsorbent is covered by a continuous monomolecular layer, P is the equilibrium pressure of the adsorbed gas, P_s is the saturated vapour pressure, and C is a constant for a given temperature. According to Eq. (20.12), $\frac{P}{V(P_s - P)}$ plotted versus $\frac{P}{P_s}$ gives a straight line with a slope $\frac{C-1}{V_m C}$.

To calculate the differential heat of adsorption \bar{Q}_A use is made of the equations

$$\bar{Q}_A = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_\theta \quad (20.13)$$

and

$$\bar{Q}_A = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{P_2}{P_1} \quad (20.14)$$

where P_1 and P_2 are the equilibrium pressures for two states at two temperatures T_1 and T_2 at the same amount Γ of the adsorbate or at the same degree of filling.

Exercises

1. In an experiment with adsorption of argon by coke at 194.7 K, the following results have been obtained:

P , Pa	31.9×10^3	130.5×10^3	290×10^3
P , mm Hg	24	98.4	218
Γ , mg/g	5	15.4	24

Calculate the constants in Langmuir's equation.

Solution. According to Langmuir's equation, Γ/Γ_∞ corresponds to the slope of the straight line representing P/Γ as a function of P , whereas $1/k\Gamma_\infty$ is the Y-intercept of this line. Calculate the values of P/Γ :

$P, \text{ Pa}$	31.9×10^3	130.5×10^3	290×10^3
P/Γ	6.4×10^3	8.7×10^3	12.1×10^3

Plot P on the abscissa and P/Γ on the ordinate. As can be seen from the plot (Fig. 39),

$$1/\Gamma = (11 - 7)/(240 - 60) = 0.0222$$

Hence, $\Gamma = 45.1/k\Gamma_\infty = 5.7 \times 10^3$. Consequently, $k = 1/5.7 \times 45 = 0.004$.

2. The volume V_m of gaseous nitrogen at $1.04 \times 10^5 \text{ Pa}$ (750 mm Hg) and 273 K, necessary to cover a silica gel matrix with a mono-

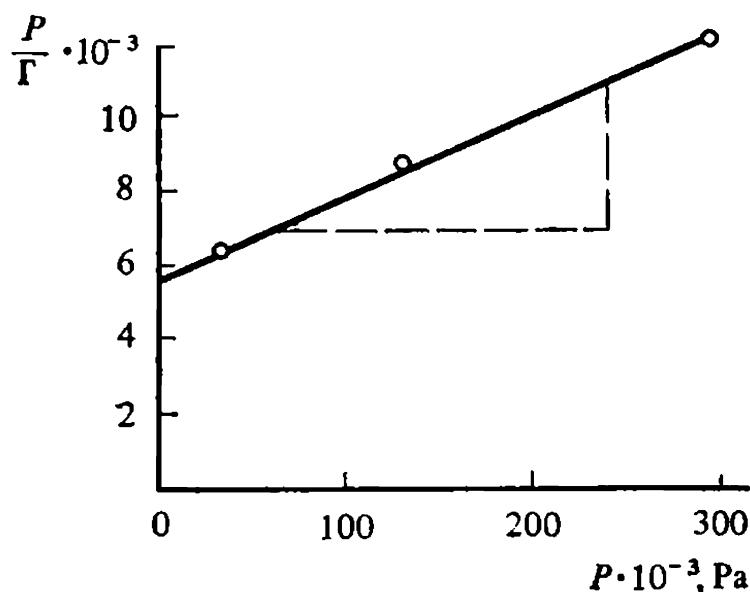


Fig. 39. P/Γ versus P curve

molecular layer, is 129 ml/g. Calculate the surface area of 1 g of silica gel if a nitrogen molecule occupies an area of $16.2 \times 10^{-20} \text{ m}^2$.

Solution. To calculate the area use the equation

$$S = \frac{(0.129 \text{ litre g}^{-1}) (6.02 \times 10^{23} \text{ mole}^{-1}) (16.2 \times 10^{-20} \text{ m}^2)}{22.4 \text{ litre mole}^{-1}} = 560 \text{ m}^2 \text{ g}^{-1}$$

3. At 77.5 K, the adsorption isotherm of krypton was taken on a silver catalyst. It is characterized by the following values:

$P, \text{ mm Hg}$	0.0992	0.1800	0.3686	0.5680	0.6843
Volume of adsorbed gas per kg of catalyst, cm^3/g	0.0127	0.0150	0.0176	0.0190	0.1980

Calculate the constants in the BET equation and the specific surface of the catalyst, assuming that the area of a krypton molecule is $s_{\text{Kr}} = 19.5 \times 10^{-20} \text{ m}^2$, the density of krypton is $d_{0^\circ\text{C}} = 3.739 \text{ g/litre}$, and the pressure of its saturated vapour is $P_s = 2.57 \text{ mm Hg}$.

Solution. Process and tabulate the experimental data:

P , mm Hg	V , cm ³ /g	P/P_s	$P_s - P$
0.0992	0.0127	0.0385	2.4708
0.1800	0.0150	0.0700	2.3900
0.3686	0.0176	0.1430	2.2014
0.5680	0.0190	0.2200	2.0020
0.6843	0.0198	0.2660	1.8857

Proceeding from these data, plot $\frac{P}{V(P_s - P)}$ versus $\frac{P}{P_s}$ (Fig. 40). Use the plot to find $\tan \alpha$:

$$\tan \alpha = \frac{C-1}{V_m - C} = 68 \quad (a)$$

The Y-intercept corresponds to $\frac{1}{V_m C} = 0.5$ (b). Solve equations (a) and (b) together to obtain the values of V_m and C : $C = 136$; $V_m =$

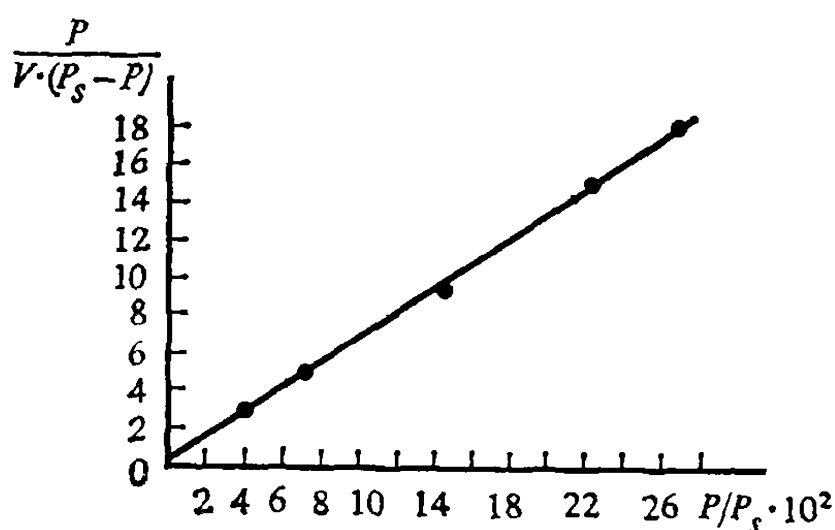


Fig. 40. $P/[V(P_s - P)]$ versus P/P_s curve

0.0146 cm³/g. In order to calculate the specific surface, refer V_m to one mole:

$$V_m = 0.0146 \text{ cm}^3/\text{g} = \frac{0.0146 \times 3.739 \times 10^{-3}}{83.6} = 6.5 \times 10^{-7} \text{ mole/g}$$

Then, the specific surface will be.

$$S_{sp} = 6.5 \times 10^{-7} \times 6.02 \times 10^{23} \times 19.5 \times 10^{-16} = 763.05 \text{ cm}^2/\text{g}$$

Problems

1. The amount of nitrogen V (referred to 273 K and 1.01×10^5 Pa) adsorbed by 1 g of activated charcoal at 273 K and different pressures is as follows:

P , Pa	51.8×10^2	16.0×10^3	33.0×10^3	45.3×10^3	74.2×10^3
V , $\text{cm}^3 \text{ g}^{-1}$	0.987	3.04	5.08	7.04	10.31

Proceeding from these values, plot Langmuir's isotherm and calculate the appropriate constants.

2. Determine the amount (in litres) of ammonia that can be adsorbed on the surface of 45 g of activated charcoal at 289 K and 1.01×10^5 Pa if the entire surface of the latter is covered with NH_3 . The surface of 1 g of activated charcoal is 1000 m^2 . The diameter of an NH_3 molecule is $3 \times 10^{-8} \text{ cm}$. The molecules touch in the same plane so that the centres of four adjacent spheres occupy the corners of a square.

3. Calculate the surface area of a catalyst which, taken in an amount of 1 g and forming a monolayer, adsorbs 103 cm^3 of nitrogen (at 1.01×10^5 Pa and 273 K). The adsorption is measured at 78 K, and the area occupied by one nitrogen molecule on the surface is $16.2 \times 10^{-20} \text{ m}^2$.

4. Calculate the constants in Langmuir's equation and x/m at 23.8×10^4 Pa (the experimental value of x/m is 30.8 mm^3) if the adsorption of nitrogen on mica depends on pressure as follows:

P , Pa	2.8×10^{-1}	6.1×10^{-1}	17.3×10^{-1}
x/m	12.0	19.0	28.2

(the ratio x/m is expressed in cubic millimetres at 293 K and 1.01×10^5 Pa, and the gas is adsorbed by 24.3 g of mica whose surface area is 5750 cm^2).

5. The specific area of activated charcoal is $400 \text{ m}^2/\text{g}$. The density of methanol at 288 K is 0.7958 g/cm^3 . Determine the maximum amount of methanol adsorbed by 1 g of charcoal at 288 K if the alcohol forms a monomolecular layer while being adsorbed.

6. Determine the constants in Langmuir's equation if the values of P and Γ at 273 K are as follows:

P , Pa	1.35×10^4	2.63×10^4	3.98×10^4	5.30×10^4
Γ , mole/g	0.150	0.275	0.380	0.470
P , Pa	6.63×10^4	7.94×10^4	9.25×10^4	1.06×10^5
Γ , mole/g	0.550	0.620	0.685	0.745

7. Determine the constants in Langmuir's equation and the adsorption of CO_2 on mica at 7 Pa if P and Γ have the following values at 155 K:

P , Pa	4.8×10^{-1}	11.9×10^{-1}	20.6×10^{-1}	41.0×10^{-1}	98.0×10^{-1}
$\Gamma \times 10^{10}$, mole/ cm^3	1.22	1.95	2.55	3.24	3.62

8. Carbon monoxide CO is adsorbed on mica at 90 K. The pressure and volume of the adsorbed gas have the following values under normal conditions:

P , Pa	75	139	600	724	1050	1400
$V \times 10^3$, cm ³	10.82	13.39	17.17	17.60	18.89	19.60

The surface area of mica is 6.24×10^3 cm². Determine the area occupied by one CO molecule.

9. Magnesium oxide adsorbs silica from water. Produce a plot in logarithmic coordinates, proceeding from the following data:

MgO, ppm	0	75	100	200
SiO ₂ residue, ppm	26.2	9.2	6.2	1.0
SiO ₂ (spec.), ppm	0	17.0	20.0	25.2

Calculate the constants in Freundlich's equation. Determine the amount of magnesium oxide (ppm) necessary to bring down the residual silica to 2.9 ppm.

10. Calculate the amount of hydrogen (measured under standard conditions) adsorbed by 100 ml of an adsorbent if the surface area of the latter is 850 m² ml⁻¹ and 95% of the surface is active. The diameter of a hydrogen molecule is 27 nm. The adsorbed molecules touch in the same plane so that the centres of four adjacent spheres occupy the corners of a square.

11. Gases A and B tend to occupy particular sites on the surface of an adsorbent. Demonstrate that the degree of filling of the surface occupied by gas molecules is

$$\theta_A = k_A P_A / (1 + k_A P_A + k_B P_B)$$

12. Calculate the specific surface of a catalyst if the adsorption of krypton at 77.5 K is characterized by the following parameters:

P , mm Hg	0.447	0.645	0.159	0.450
Volume of gas adsorbed by 1 g of catalyst, cm ³ /g	0.4185	0.4619	0.5234	0.6313

The catalyst weighs 13.03 g. The area occupied by one krypton molecule is $s_{\text{Kr}} = 19.2 \times 10^{-20}$ m², the density of krypton is $d_{0^\circ\text{C}} = 3.739$ g/litre, and the pressure of its saturated vapour is $P_s = 2.57$ mm Hg (342.65 Pa).

13. At 298 K, the adsorption isotherm of benzene was taken on activated charcoal with the following parameters:

P/P_s	0.1	0.2	0.3	0.4	0.5	0.6
$\frac{P}{V(P_s - P)}$	0.19	0.23	0.35	0.42	0.5	0.6

The density of benzene is $d_{20^\circ\text{C}} = 0.878$ g/litre, and the area occupied by a benzene molecule in the monolayer is $s_{\text{C}_6\text{H}_6} = 30.3 \times 10^{-16}$ cm². Calculate the specific surface of activated charcoal.

14. At 77.5 K, the adsorption isotherm of krypton was taken on a platinum catalyst with the following parameters:

P , mm Hg	0.149	0.200	0.308	0.491
Volume of gas adsorbed by 1 g of catalyst, cm^3/g	0.2763	0.3040	0.3524	0.4098

Calculate the constants in the BET equation and the specific surface of the catalyst if the area occupied by a krypton molecule is $s_{\text{Kr}} = 19.2 \times 10^{-20} \text{ m}^2$, the density of krypton is $d_{0^\circ\text{C}} = 3.739 \text{ g/litre}$, and the pressure of its saturated vapour is $P_s = 2.57 \text{ mm Hg}$ (342.65 Pa).

15. The pressure measured during adsorption of a certain amount of NH_3 by 1 g of charcoal is $1.4 \times 10^4 \text{ Pa}$ at 303 K and $7.44 \times 10^4 \text{ Pa}$ at 353 K. Calculate the heat of adsorption at a given degree of filling.

16. Under normal conditions, 40 cm^3 of CO_2 are adsorbed by 1 g of charcoal at 303 K and $8 \times 10^4 \text{ Pa}$ and at 273 K and $2.27 \times 10^4 \text{ Pa}$. Determine the heat of adsorption.

17. Determine the heat of adsorption of nitrogen oxide on barium fluoride proceeding from the following data:

233 K		273 K	
P , Pa	Γ , cm^3	P , Pa	Γ , cm^3
3.53×10^3	3.17	7.51×10^3	1.81
4.65×10^3	3.70	11.15×10^3	2.40
6.70×10^3	4.40	17.3×10^3	3.01
8.55×10^3	5.09	23.9×10^3	3.73
12.5×10^3	6.14	33.9×10^3	4.24
17.3×10^3	6.70	44.0×10^3	5.30
18.6×10^3	7.35	53.0×10^3	5.86
30.3×10^3	8.48	59.0×10^3	6.16
35.3×10^3	9.07	60.7×10^3	6.34
47.3×10^3	9.92	82.0×10^3	7.30

18. Determine the heat of adsorption of N_2 , CO , CH_4 , CO_2 , and NH_3 on charcoal if that of hydrogen is $10.46 \times 10^3 \text{ J/mole}$. The boiling points of the above substances are as follows:

Substance	H_2	N_2	CO	CH_4	CO_2	NH_3
T , K	20.4	77.3	83.1	111.7	194.6	240.0

Use the approximate condition

$$\Delta H/T_{\text{n.b.}} = \text{const}$$

Multivariant Problem

The amount V of substance (referred to 273 K and 1.01×10^5 Pa (1 atm)) adsorbed by 1 g of an adsorbent at 273 K and different pressures is given in the table: (1) plot the adsorption isotherm $V = f(P)$ and $P/V = f(P)$; (2) express the adsorption isotherm in terms of Langmuir's equation; (3) determine the amount of adsorption (m^3/g) at the maximum degree of filling of the adsorbent; (4) determine the degree of filling of the adsorbent at pressure P ; and (5) determine the gas pressure at which the degree of filling of the adsorbent will be 0.4.

Vari- ant	T, K	Adsorbent	Adsorbate	$P_1 \times 10^{-4}$, Pa	$P \times 10^{-3}$, Pa	$V \times 10^6$, m^3/g
1	273	Charcoal	N_2	2.0	1.62	0.31
					5.30	0.99
					17.30	3.04
					30.70	5.10
					44.50	6.90
2	273	Charcoal	CO_2	2.0	4.20	12.73
					8.10	21.20
					11.70	26.40
					16.50	32.20
					24.00	38.60
3	273	Charcoal	CO	5.0]	9.80	2.53
					24.20	5.57
					41.30	8.43
					60.00	11.20
					72.50	12.85
4	273	Charcoal	NH_3	5.0	10.50	60.40
					21.60	90.30
					42.70	115.70
					65.60	127.00
					85.20	132.40
5	273	BaF_2	CO	5.0	11.30	2.04
					24.40	3.72
					44.50	5.30
					61.00	6.34
					82.50	7.30

Vari- ant	T, K	Adsorbent	Adsorbate	$P_1 \times 10^{-4}$, Pa	$P \times 10^{-3}$, Pa	$V \times 10^6$, m ³ /g
6	273	Charcoal	H ₂	2.0	27.60	0.447
					43.40	0.698
					57.40	0.915
					72.20	1.142
					86.10	1.352
7	194.5	Charcoal	N ₂	2.7	1.67	3.47
					8.83	13.83
					20.00	23.00
					36.30	27.94
					52.00	33.43
8	194.5	Charcoal	CH ₄	5.0	25.6	15.2
					36.7	19.1
					47.8	22.3
					60.5	25.3
					77.0	28.4
9	194.5	Charcoal	CO	0.5	4.00	15.80
					5.34	19.05
					9.65	27.70
					16.65	34.10
					19.80	38.95
10	194.5	Charcoal	Ar	3.0	3.22	5.09
					7.25	10.02
					13.15	15.56
					17.25	18.81
					39.50	29.14
11	273	Charcoal	C ₂ H ₄	5.0	9.35	39.5
					12.45	42.8
					22.50	49.9
					42.60	56.5
					82.50	64.5
12	293	Charcoal	C ₂ H ₄	2.0	2.00	10.4
					4.27	20.8
					10.57	30.5
					29.50	42.4
					91.50	55.2

Complex Problems

- Determine the equilibrium constant K_P of reaction (A) at 298 K and in the range of temperatures from 300 to 1000 K at 100 degree intervals.
- Plot $K_P = f(T)$ for temperatures ranging from 198 to 1000 K.
- Plot $\log K_P$ versus $1/T$ for temperatures ranging from 298 to 1000 K.
- For a given reaction, plot the yield x of the end product versus the equilibrium constant, provided the initial mixture is stoichio-metric.
- Determine the yield of the reaction product at temperatures ranging from 298 to 1000 K if the pressure of the equilibrium mixture is 1.0133×10^5 Pa and plot the yield of the end product versus temperature at the above pressure.
- Draw a conclusion as regards the shift of equilibrium if added to the initial mixture is nitrogen which does not participate in the reaction.
- Determine the activity coefficient of the substances involved in the reaction at 2.0×10^7 Pa and at the temperature corresponding to the maximum yield of the reaction products if the equilibrium pressure is 1.0133×10^5 Pa.
- Calculate K_γ at the temperature corresponding to the maximum yield of the reaction products and at 2.0×10^7 Pa.
- Calculate the equilibrium yield of the reaction products at 2.0×10^7 Pa.
- Determine the heat of transition from the initial to the equilib-rium state at temperatures ranging from 300 to 1000 K and plot $Q_P = f(T)$.
- Determine the partial pressures of the gases in the system in the state of equilibrium, provided the yield of the reaction products is maximum at the equilibrium pressure of 2.0×10^5 Pa.
- Determine the temperature to which the equilibrium system is to be cooled for one of the reactants to start condensing from it.

Variant	Reaction (A)	Variant	Reaction (A)
1	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$	4	$2\text{CH}_4 + \text{O}_2 = 2\text{CO} + 4\text{H}_2$
2	$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$	5	$2\text{CH}_4 = \text{CH} \equiv \text{CH} + 3\text{H}_2$
3	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	6	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$

CHAPTER 21

Formal Kinetics

Basic Equations and Symbols

For reactions given by the stoichiometric equation



the true rate w is expressed as the following relation:

$$w = -\frac{1}{\nu_{A_1}} \frac{dc_{A_1}}{dt} = -\frac{1}{\nu_{A_2}} \frac{dc_{A_2}}{dt} = \dots = \frac{1}{\nu_{B_1}} \frac{dc_{B_1}}{dt} = \frac{1}{\nu_{B_2}} \frac{dc_{B_2}}{dt} \quad (21.1)$$

in which ν_{A_i} and ν_{B_i} are stoichiometric coefficients, A stands for the initial substances, and B stands for the reaction products.

The relationship between the reaction rate and concentration of the initial substances (differential form of the kinetic equation) is expressed in terms of the mass action law

$$w = kc_{A_1}^{n_1}c_{A_2}^{n_2} \quad (21.2)$$

where k is the reaction rate constant, and n_1, n_2, \dots are numbers representing the particular order of the reaction relative to component A_1, A_2, \dots , respectively. The overall order n of the reaction is

$$n = n_1 + n_2 \quad (21.3)$$

The mean reaction rate \bar{w} is

$$\bar{w} = (c_2 - c_1)/(t_2 - t_1), \quad (21.4)$$

where $(t_2 - t_1)$ is the time interval during which the reactant concentration changes from c_1 to c_2 in the course of the reaction. For different types of reactions, the mass action law will take different forms. In the case of a zeroth-order reaction, the differential forms of the kinetic equation become

$$-\frac{dc_{A_i}}{dt} = k \quad (21.5)$$

$$\frac{dx}{dt} = k \quad (21.6)$$

and the integral forms of the kinetic equation will be as follows:

$$k = (c_{0, A_i} - c_{A_i})/t \quad (21.7)$$

$$k = x/t \quad (21.8)$$

$$c_{A_i} = c_{0, A_i} - kt \quad (21.9)$$

$$t_{1/2} = 0.5c_{0, A_i}/k \quad (21.10)$$

where c_{0, A_i} is the initial concentration of reactant A_i , c_{A_i} is the concentration of reactant A_i at instant t , x is the number of moles of substance A, which have reacted by instant t , $x = c_{0, A_i} - c_{A_i}$, and $t_{1/2}$ is the half-life (time period during which the concentration of the substance becomes half the initial one).

In the case of first-order reactions ($A \rightarrow$ products), the differential forms of the kinetic equation become

$$-\frac{dc_A}{dt} = kc_A \quad (21.11)$$

$$\frac{dx}{dt} = k(c_{0, A} - x) \quad (21.12)$$

and the integral forms of the kinetic equation become

$$k = \frac{2.3}{t} \log \frac{c_{0, A}}{c_A} \quad (21.13)$$

$$k = \frac{2.3}{t} \log \frac{c_{0, A}}{c_{0, A} - x} \quad (21.14)$$

$$c_A = c_{0, A} e^{-kt} \quad (21.15)$$

$$t_{1/2} = 0.693/k \quad (21.16)$$

In the case of second-order reactions ($A_1 + A_2 \rightarrow$ products), if the initial concentrations of the reactants are the same, $c_{0, A_1} = c_{0, A_2}$, the differential forms of the kinetic equation are

$$-\frac{dc}{dt} = kc^2 \quad (21.17)$$

$$\frac{dx}{dt} = k(c_{0, A} - x)^2 \quad (21.18)$$

while the integral forms are

$$k = \frac{1}{t} \left(\frac{1}{c_A} - \frac{1}{c_{0, A}} \right) \quad (21.19)$$

$$k = \frac{1}{t} \frac{x}{c_{0, A} (c_{0, A} - x)} \quad (21.20)$$

$$c_A = \frac{c_{0, A}}{c_{0, A} kt + 1} \quad (21.21)$$

$$t_{1/2} = \frac{1}{kc_{0, A}} \quad (21.22)$$

If the reactant concentrations in second-order reactions ($A_1 + A_2 \rightarrow$ products) are dissimilar, $c_{0, A_1}^* \neq c_{0, A_2}$, then the differential forms

* Sometimes the initial concentrations c_{0, A_1} are denoted by the letter a and c_{0, A_2} , by the letter b .

of the kinetic equation are

$$-\frac{dc}{dt} = kc_{A_1}c_{A_2} \quad (21.23)$$

$$\frac{dx}{dt} = k(c_{0,A_1} - x)(c_{0,A_2} - x) \quad (21.24)$$

and the integral forms of the kinetic equation will be

$$k = \frac{2.3}{t} \frac{1}{c_{0,A_1} - c_{0,A_2}} \log \frac{c_{A_1}c_{0,A_2}}{c_{A_2}c_{0,A_1}} \quad (21.25)$$

and

$$k = \frac{2.3}{t} \frac{1}{c_{0,A_1} - c_{0,A_2}} \log \frac{(c_{0,A_1} - x)c_{0,A_2}}{(c_{0,A_2} - x)c_{0,A_1}} \quad (21.26)$$

In the case of third-order reactions ($A_1 + A_2 + A_3 \rightarrow$ products), if the initial reactant concentrations are equal, $c_{0,A_1} = c_{0,A_2} = c_{0,A_3}$, the differential forms of the kinetic equation become

$$-\frac{dc_A}{dt} = kc_A^3 \quad (21.27)$$

$$\frac{dx}{dt} = k(c_{0,A} - x)^3 \quad (21.28)$$

and the integral forms are

$$k = \frac{1}{2t} \left(\frac{1}{c_{A_1}^2} - \frac{1}{c_{0,A_1}^2} \right) \quad (21.29)$$

$$k = \frac{1}{2t} \left[\frac{1}{(c_{0,A_1} - x)^2} - \frac{1}{c_{0,A_1}^2} \right] \quad (21.30)$$

$$t_{1/2} = \frac{3}{2kc_{0,A_1}^2} \quad (21.31)$$

One way to determine the order of a reaction is by the Ostwald-Noyes (integral) method:

$$n_i = \frac{\log(t'_{1/2}/t''_{1/2})}{\log(c_{0,2}/c_{0,1})} + 1 \quad (21.32)$$

where $t'_{1/2}$ is the half-life corresponding to the initial concentration $c_{0,1}$, and $t''_{1/2}$ is the half-life corresponding to the initial concentration $c_{0,2}$. (Instead of the time period during which half the substance is spent in the reaction ($t_{1/2}$), one may take the time it takes one third of the substance to react ($t_{1/3}$) or one fifth ($t_{1/5}$), etc.)

Another way to determine the reaction order is by the van't Hoff (differential) method:

$$n_i = (\log w_1 - \log w_2)/(\log c_{0,1} - \log c_{0,2}) \quad (21.33)$$

where w_1 and w_2 are the true reaction rates corresponding to the initial concentrations $c_{0,1}$ and $c_{0,2}$, respectively, and n_i is the particular order with respect to the component whose initial concentration is c_0 .

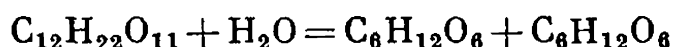
Exercises

1. The transformation of benzoyl peroxide into diethyl ether (first-order reaction) at 333 K was 75.2% complete within 10 min. Calculate the reaction rate constant.

Solution. Write a first-order equation and substitute the appropriate numerical values into it:

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) = \frac{2.303}{10} \log \frac{100}{24.8} = 0.2303 \log 0.43 \\ = 0.2303 \times 0.606 = 0.140 \text{ min}^{-1}$$

2. In the presence of ions H^+ , cane sugar (biose) is hydrolyzed with water, dissociating into two monoses (glucose and fructose) according to the equation



The cane sugar solution rotates the polarization plane to the right, and the mixture of glucose with fructose rotates it to the left. In both cases, the rotation angle is proportional to the concentration of the solutes. At 298 K, the change in the angle α of rotation of the polarization plane of the cane sugar solution in 0.5 N HCl with a large amount of water with time was as follows:

t , min	0	176	∞
α , deg	25.16	5.46	-8.38

Calculate the reaction rate constant and the amount of sugar (%) inverted within 236 min. Determine the rotation angle by $t = 236$ min.

Solution. Denote the rotation angle at the initial moment by α_0 , α_∞ after the inversion is over, and α_t when observed at a given point in time. Since the change in the rotation angle from the initial to final moment is $\alpha_0 - \alpha_\infty$, this quantity is proportional to the initial sugar concentration $c_{0,A}$, whereas the sugar concentration at a given moment, $c_{0,A} - x$, is proportional to the change in the rotation angle from a given moment, α_t , to the end of inversion, α_∞ , that is it is proportional to $\alpha_t - \alpha_\infty$. The reaction of sugar inversion in the presence of a large amount of water is of the first order. Calculate the rate constant of the reaction using Eq. (21.14) with $c_{0,A}$ and $c_{0,A} - x$ being substituted by the proportional quantities $\alpha_0 - \alpha_\infty$ and $\alpha_t - \alpha_\infty$:

$$k_1 = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

Substitution of the numerical values of t , α_0 , α_∞ , and α_t into the equation gives

$$k_1 = \frac{2.303}{176} \log \frac{25.16 - (-8.38)}{5.46 - (-8.38)} = \frac{2.303}{177} \log \frac{33.54}{13.84} = 0.005028$$

Determine the amount of sugar inverted within 236 min. To do this, substitute 0.005028 and 236 min for k_1 and t , respectively, in Eq. (21.14). Then,

$$\log \frac{c_{0,A}}{c_{0,A} - x} = \frac{0.005028 \times 236}{2.303} = 0.5152$$

This gives us the quantity of hydrolyzed sugar:

$$\frac{c_{0,A}}{c_{0,A} - x} = 3.275 \text{ and } x = 0.6948c_{0,A} \text{ or } x = 0.6948 \times 100 = 69.48\%$$

Now determine the rotation angle corresponding to $t = 236$ min. When all of the initial amount of sugar has been inverted, the change in the rotation angle will be $25.16^\circ - (-8.38^\circ) = 33.54^\circ$. Since at $t = 236$ min 30.52% of sugar remain unhydrolyzed, the change in the rotation angle, caused by the transformation of this amount, will be less accordingly. Denote this change by z , then,

$$\frac{z}{33.54} = \frac{30.52}{100}, \quad z = \frac{33.54 \times 30.52}{100} = 10.23^\circ$$

Since $z = \alpha_t - (-8.38^\circ)$, then $\alpha_t = z - 8.38^\circ = 10.23^\circ - 8.38^\circ = +1.85^\circ$, that is 236 min after the onset of the reaction, the reaction mixture will rotate to the right through an angle of 1.85° .

3. For the reaction $A = B + C + D$, proceeding in the gas phase at $v = \text{const}$, the total pressure at the initial moment $t = 0$, $P = P_0$ has been determined, and after $t = t'$, $P = P'$. Express the rate constant in terms of the total pressure, assuming that the reaction is of the first order.

Solution. According to the equation for ideal gases, $c_A = P_A/RT$, then,

$$k = (2.3/t) \log (P_{0,A}/P_A)$$

Express the partial pressures P_A of substance A in terms of the total pressure P . To this end, write, according to Dalton's equation, $P = P_A + P_B + P_C + P_D$; introduce the quantity x (decrease in the pressure of substance A during the reaction), then $P_A = P_{0,A} - x$. The initial pressure in the system equals the pressure of substance A: $P_{0,A} = P_0$. Write $P_B = P_C = P_D = x$. In that case, the total pressure at instant t will be $P = P_0 - x + 3x = P_0 + 2x$. Express x in terms of P and P_0 : $x = (P - P_0)/2$. Substitute the value of x into the equation $P_A = P_0 - x$ and express the partial

pressure of reactant A in terms of the total pressure:

$$P_A = \frac{3P_0 - P}{2} \text{ and } k = \frac{0.3}{t} \log \frac{2P_0}{3P_0 - P}$$

4. In the course of the reaction $\text{CH}_3\text{COOCH}_{3(g)} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 + \text{CO}$, the total pressure changes as follows:

t , min	0	6.5	13.0	19.9
P , Pa	41 489.6	54 386.6	65 050.4	74 914.6

Demonstrate that the reaction is of the first order and calculate the mean value of the rate constant at the experimental temperature of 298 K ($V = \text{const}$).

Solution. If the reaction is of the first order, its rate constant, calculated in accordance with the equation $k = 1/t \ln (c_0 - c)$, must remain constant at any point in time. In the mathematical equation, the initial substance concentrations at the initial and current moments may be replaced by the partial pressures of the substance at the same moments because the pressure of a gas is proportional to its concentration (at $T = \text{const}$). The above pressures (except for the first one) represent the total pressure of all four gases, and to calculate the rate constant one must know only the acetone pressure.

Let, at moment t , $P_{\text{C}_2\text{H}_4} = x$, then $P_{\text{H}_2} = P_{\text{CO}} = x$ and $P_{(\text{CH}_3)_2\text{COO}} = P_0 - x$, P_0 being the initial pressure of acetone. The total pressure at any moment is $P = P_0 - x + 3x = P_0 + 2x$, then

$$x = \frac{P - P_0}{2}, \quad P_0 - x = \frac{3P_0 - P}{2}$$

Substitute the pressure ratio for that of concentrations:

$$\frac{c_0}{c} = \frac{P_0}{P_0 - x} = \frac{2P_0}{3P_0 - P}$$

then

$$k = \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P}$$

Substitute the values of pressure in the system for a given point in time and calculate the rate constant:

$$k = \frac{2.303}{6.5} \log \frac{2 \times 41\,589.6}{3 \times 41\,589.6 - 54\,386.4} = 0.0256$$

$$k = \frac{2.303}{13.0} \log \frac{2 \times 41\,589.6}{3 \times 41\,589.6 - 65\,050.4} = 0.0255$$

$$k = \frac{2.303}{19.9} \log \frac{2 \times 41\,589.6}{3 \times 41\,589.6 - 74\,914.6} = 0.0257$$

$$k_{\text{mean}} = 0.0256$$

The rate constant is invariable within the inevitable experimental errors. Consequently, this reaction is of the first order.

5. The rate of reaction:



in the presence of nitrobenzene was determined at 298 K under the following conditions:

$t, \text{ s}$	1200	1800	2400	3600	4500	5400
$x, \text{ mole/litre}$	0.00876	0.01065	0.01208	0.01392	0.01476	0.01538

where t is time and x is the amount of triethylamine or methyl iodide reacted within the time t . The initial concentrations of the amine and alkyl iodide are 0.0198 mole/litre. The reaction is of the second order. Determine its rate constant.

Solution. For a second-order reaction involving two substances in the same concentrations,

$$k = \frac{x}{ta(a-x)}, \quad k = \frac{0.00876}{1200 \times 0.0198 \times 0.01104} = 0.0334$$

$k = 0.0334, 0.0327, 0.0329, 0.0332, 0.0328$, and 0.0325 . The mean value is $k = 0.0329 \text{ litre mole}^{-1} \text{ s}^{-1}$.

6. The rate constant of the reaction of saponification of ethyl acetate with sodium hydroxide at 283 K is 2.38 if the concentration is given in mole/litre and time is given in minutes. Calculate the time necessary for saponification of 50% of ethyl acetate if 1 m³ of a 0.05 *N* solution of ethyl acetate is mixed, at 289 K, with (a) 1 m³ 0.05 *N* NaOH, (b) 1 m³ 0.1 *N* NaOH, and (c) 1 m³ 0.04 *N* NaOH.

Solution. The concentrations of the acetic ester and alkali are equal; therefore, Eq. (21.20) should be used:

$$t = \frac{1}{k_2 c_{0,1}} \frac{x}{(c_{0,A_1} - x)}$$

Since the mixture volume is 2 m³, then $c_{A_1} = 0.025 \text{ g-equiv/litre}$ and $x = 0.0125 \text{ g-equiv/litre}$. Substitution of these values and k_2 into the equation for t gives

$$t_1 = \frac{1}{2.38} \frac{0.0125}{0.025(0.025 - 0.0125)} = \frac{1}{2.38} \frac{0.0125}{0.025 \times 0.0125} = 16.8 \text{ min}$$

The concentration of the ester is not equal to that of the alkali, that is the reactants are taken in different amounts, therefore, use Eq. (21.26):

$$t = \frac{2.303}{k_2} \frac{1}{c_{0,A_1} - c_{0,A_2}} \log \frac{(c_{0,A_1} - x) c_{0,A_2}}{(c_{0,A_2} - x) c_{0,A_1}}$$

If the initial ester concentration is denoted by c_{0,A_1} and that of the alkali by c_{0,A_2} , then $c_{0,A_1} = 0.025 \text{ g-equiv/litre}$, $c_{0,A_2} = 0.05 \text{ g-equiv/}$

litre, and $c_x = 0.0125$ g-equiv/litre. Substitution of these values into the equation for t gives

$$t_2 = \frac{2.303}{2.38} \frac{1}{0.025 - 0.05} \log \frac{(0.025 - 0.0125) 0.05}{(0.05 - 0.0125) 0.025} = 6.81 \text{ min}$$

The ester concentration is $c_{0,A_1} = 0.025$ g-equiv/litre, $c_{A_1} = 0.0125$ g-equiv/litre, and the alkali concentration is $c_{0,A_2} = 0.02$ g-equiv/litre. Then,

$$t_3 = \frac{2.303}{2.38} \frac{1}{0.025 - 0.02} \log \frac{(0.025 - 0.0125) 0.02}{(0.02 - 0.0125) 0.025} = 24.2 \text{ min}$$

7. The rate constant of the reaction $A \rightarrow B$ is $k = 0.5$, the initial concentration of A being $c_{0,A} = 1$ mole/litre. Calculate the degree of conversion of substance A within $t = 1$ h if the reaction is of the zeroth, first, and second order. How is the degree of conversion dependent on the order of the reaction?

Solution. For the zeroth-order reaction, according to Eq. (21.7),

$$0.5 = \frac{1\alpha}{1}, \quad \alpha = 0.5$$

For the first-order reaction, according to Eq. (21.14),

$$0.5 = \frac{2.3}{1} \log \frac{1}{1-x}, \quad \frac{0.5}{2.3} = -\log(1-\alpha), \quad \alpha = 0.39$$

For the second-order reaction, according to Eq. (21.20),

$$0.5 = \frac{1}{1} \left(\frac{1}{c_0(1-x)} - \frac{1}{c_0} \right), \quad 0.5 = \frac{1}{1-\alpha}, \quad \alpha = 0.33$$

The higher the reaction order, the lower the degree of conversion and the slower the reaction.

8. A solution of ethyl acetate is saponified at $c_{0,1} = 0.01$ g-equiv/litre and 293 K, with 0.002 g-equiv/litre ($c_{0,2}$) of a sodium hydroxide solution within $t_1 = 23$ min, the degree of saponification being 10%. How much time will it take (t_1 , t_2 , etc.) for the same acetic ester solution to be saponified to the same degree with NaOH solutions of the following concentrations: $c_{0,3} = 0.004$, $c_{0,4} = 0.006$, $c_{0,5} = 0.008$, and $c_{0,6} = 0.01$ g-equiv/litre?

Solution. Using the following notation: $a = c_{0,1}$, $b = c_{0,2}$, and $x = 0.1c_{0,1}$ in Eq. (21.26) gives

$$\begin{aligned} k &= \frac{1}{t} \frac{2.3}{(c_{0,1} - c_{0,2})} \log \frac{(c_{0,1} - 0.1c_{0,1}) c_{0,2}}{(c_{0,2} - 0.1c_{0,1}) c_{0,1}} \\ &= \frac{2.3}{23(0.01 - 0.002)} \log \frac{(0.01 - 0.1 \times 0.01) 0.002}{(0.002 - 0.1 \times 0.01) 0.001} = 3.19 \end{aligned}$$

Substitute the value of k and those of $c_{0,3}$, $c_{0,4}$, $c_{0,5}$, and $c_{0,6}$ for $c_{0,2}$ into the equation to calculate t_2 , t_3 , t_4 , and t_5 :

$$3.19 = \frac{2.3}{t_2(0.01 - 0.004)} \log \frac{(0.01 - 0.1 \times 0.01) 0.004}{(0.004 - 0.1 \times 0.01) 0.01}$$

$$t_2 = 95 \text{ min, and so on}$$

9. The kinetics of the reaction between thiosulphate and n -propyl bromide, $\text{S}_2\text{O}_3^{2-} + \text{RBr} \rightarrow \text{RSSO}_3^- + \text{Br}^-$, was studied at 310.5 K. The concentration of ion $\text{S}_2\text{O}_3^{2-}$ was determined at different time intervals t by titration. Used for the titration were V ml of a 0.02572 N solution of I_2 per aliquot (10.02 ml) of the reaction mixture. The initial concentration of thiosulphate which was present in an excess amount was 0.100 mole/litre. The values of t and V were as follows:

t , s	0	1110	2010	3192	5052	7380	11 232	78 840
V , ml	37.63	35.20	33.63	31.90	29.86	28.04	26.01	22.24

Calculate the rate constant of the second-order reaction.

Solution. For a second-order reaction,

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where a is the concentration of $\text{S}_2\text{O}_3^{2-}$ at $t = 0$

$$a = \frac{V \times 0.02572}{V_{\text{S}_2\text{O}_3^{2-}}} = \frac{37.62 \times 0.02572}{10.02} = 0.0967 \text{ mole/litre}$$

By the time $t = 0$, a certain amount of $\text{S}_2\text{O}_3^{2-}$ has already been spent, therefore, the concentration of $\text{S}_2\text{O}_3^{2-}$ will be below the initial one (0.100 mole/litre). Calculate the initial concentration of $n\text{-C}_3\text{H}_7\text{Br}$, assuming that equilibrium is reached at $t = 78\,840$ s:

$$b = \frac{\text{total amount of } \text{S}_2\text{O}_3^{2-} \text{ spent for } n\text{-C}_3\text{H}_7\text{Br}}{V_{n\text{-C}_3\text{H}_7\text{Br}}}$$

$$= \frac{(37.63 - 22.24) 0.02572}{10.02} = 0.0395 \text{ mole/litre}$$

Calculate the concentrations of the reactants at $t = 1110$ s:

$$(b-x) = \frac{\text{amount of } \text{S}_2\text{O}_3^{2-} \text{ spent for } n\text{-C}_3\text{H}_7\text{Br}}{V_{n\text{-C}_3\text{H}_7\text{Br}}}$$

$$= \frac{(35.20 - 22.24) 0.02572}{10.02} = \frac{12.96 \times 0.02572}{10.02} \text{ mole/litre}$$

$$(a-x) = \frac{\text{amount of iodine spent for } \text{S}_2\text{O}_3^{2-}}{V_{\text{S}_2\text{O}_3^{2-}}} = \frac{35.20 \times 0.02572}{10.02} \text{ mole/litre}$$

where $(b - x)$ is the concentration of $n\text{-C}_3\text{H}_7\text{Br}$ at t , and $(a - x)$ is the concentration of $\text{S}_2\text{O}_3^{2-}$ at t . Then,

$$\frac{b(a-x)}{a(b-x)} = \frac{0.0395(35.20 \times 0.02572)/10.02}{0.0967(12.96 \times 0.02572)/10.02} = \frac{0.0395 \times 35.20}{0.0967 \times 10.96} = 1.110$$

The difference between the initial concentrations of the reactants is

$$a - b = 0.0967 - 0.0395 = 0.0572 \text{ mole/litre}$$

Consequently, the reaction rate constant will be

$$k = 0.0363 \log 1.110 = 0.0363 \times 0.0453 = 0.001644$$

$$k = 0.001644, 0.001644, 0.001649, 0.001636, 0.001618, 0.001618$$

The mean value of k is $0.001635 \text{ litre mole}^{-1} \text{ s}^{-1}$.

10. Hydrogen peroxide dissociates in an aqueous solution according to the equation $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. The kinetics of this reaction was studied by titration of samples of equal size with potassium permanganate. Determine the order of the reaction by all possible methods and calculate the mean rate constant for this reaction, proceeding from the following data:

Elapsed time, min	0	5	10	15	20	30	40
Amount of 0.0015M KMnO_4 spent for titration of $2 \times 10^{-6} \text{ m}^3$ of sample, cm^3	23.6	18.1	14.8	12.1	9.4	5.8	3.7

Solution. Determine the order of the reaction and calculate its rate by the integral graphical method assuming that the reaction may be of the first or second order. The volume of the permanganate solution spent for the titration is directly proportional to the hydrogen peroxide concentration $c_{\text{H}_2\text{O}_2} \approx V_{\text{KMnO}_4}$. Here are the data necessary for plotting:

t , min	0	5	10	15	20	30	40
V , cm^3	23.6	18.1	14.8	12.1	9.4	5.8	3.7
$(1/V) \times 10^2$	4.3	5.5	6.7	8.3	10.6	17.0	27.0
$\log (V_0/V) \times 10$		1.15	2.03	2.90	3.99	6.09	8.05

Figure 41a represents $(1/V) = f(t)$ (curve 2) and $\log (V_0/V) = f(t)$ (curve 1). The fact that $\log (V_0/V) = f(t)$ is a straight line suggests that the reaction under consideration is of the first order.

To calculate the rate constant use the equation $k = \tan \alpha \times 2.3 = \frac{1 \times 2.3}{50} = 0.046 \text{ min}^{-1}$. Check the result again by finding the derivative $\frac{dV}{dt}$ on the $V = f(t)$ plot (Fig. 41b) and calculating the rate constant with the aid of Eq. (21.1), $dV/dt = kV$. For $t = 20 \text{ min}$, the volume of potassium permanganate is $V = 9.4 \text{ cm}^3$. Determine the above derivative from the straight line on the kinetic

plot:

$$\frac{dV}{dt} = \tan \alpha = 0.439, \text{ hence, } k = \frac{0.439}{9.4} = 4.64 \times 10^{-1} \text{ min}^{-1}.$$

11. To study the dissociation of oxalic acid in concentrated sulphuric acid at 323 K there was prepared a 1/40 *M* solution of oxalic acid in 99.5% sulphuric acid. The mixture was sampled at time

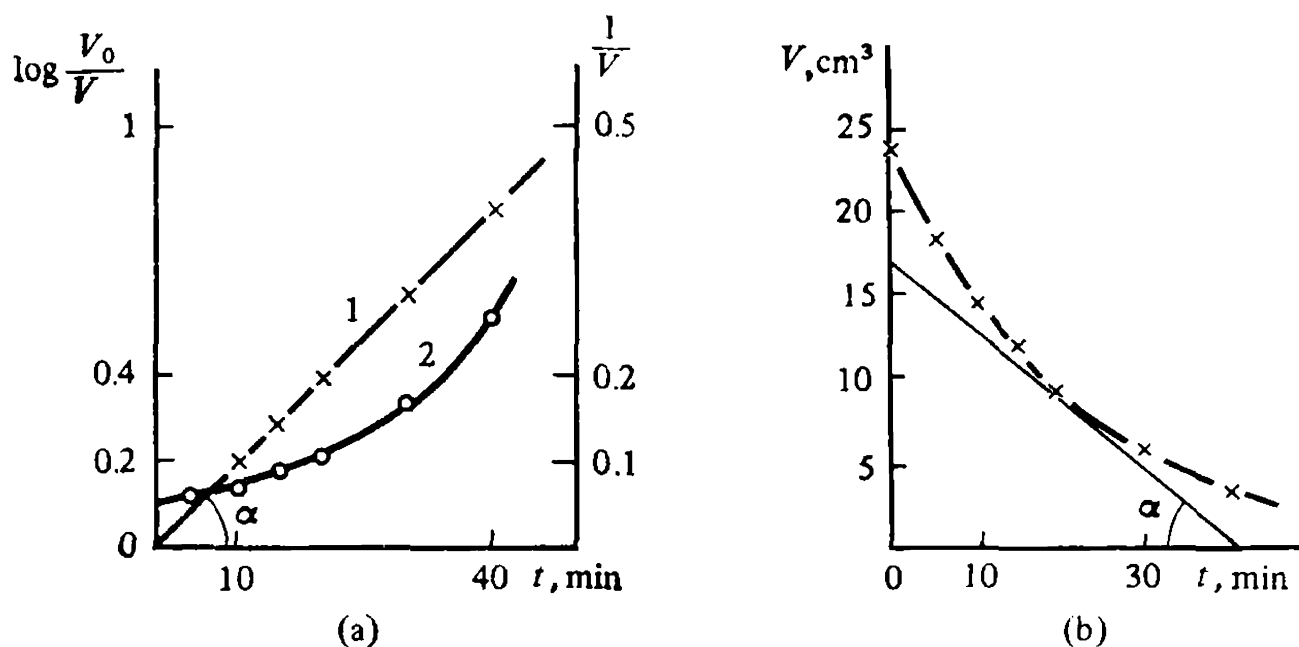


Fig. 41. Amount of potassium permanganate spent in titration versus reaction time

intervals t , and the volume V of the potassium permanganate solution necessary for titration of 10 ml $\text{H}_2\text{C}_2\text{O}_4$ was determined:

t , min	0	120	240	420	600	900	1440
V , ml	11.45	9.63	8.11	6.22	4.79	2.97	1.44

Determine the order of the reaction and its rate constant.

Solution. Assume that the reaction is of the first order:

$$k = \frac{1}{t} \ln \frac{c_0}{c}, \quad k = \frac{2.303}{120} \log \frac{11.45}{9.63} = 0.00144$$

$$k = 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140$$

The mean value of k is 0.00145 min^{-1} .

12. To study the interaction between ions Br^- and ClO^- , $\text{ClO}^- + \text{Br}^- \rightarrow \text{BrO}^- + \text{Cl}^-$, at 298 K, 100 ml of 0.1 *N* NaClO were mixed with 48 ml of 0.5 *N* NaOH and 21 ml of distilled water. Added to the mixture were 81 ml of a 1% potassium bromide solution. The mixture was sampled at time intervals t for determination of the BrO^- content with the following results:

t , min	0	3.56	7.65	15.05	26.00	47.60	90.60
BrO^- concentration $\times 10^{-2}$ mole/litre	0	0.0560	0.0953	0.1420	0.1800	0.2117	0.2360

The NaClO and KBr concentrations in the reaction mixture at $t = 0$ were 0.003230 and 0.002508 mole/litre, respectively, the pH of the solution being 11.28. Determine the order of the reaction and its rate constant.

Solution. Assume that the reaction is of the second order:

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}, \quad a = [\text{NaClO}]_0 = 0.003230$$

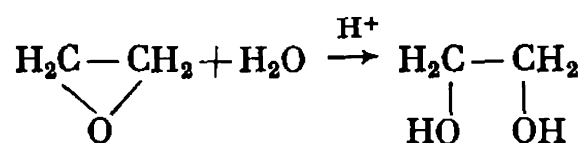
$$b = [\text{KBr}]_0 = 0.002508, \quad a - b = 0.000722$$

$$k = \frac{2.303}{3.56 \times 7.22 \times 10^{-4}} \log \frac{2.508 \times 10^{-3} (0.003230 - 0.000560)}{3.230 \times 10^{-3} (0.002508 - 0.000560)} = 23.42 \text{ litre mole}^{-1} \text{ min}^{-1}$$

$$k = 23.42, 23.30, 23.52, 23.90, 23.80, 23.80$$

The mean value of k is $23.62 \text{ litre mole}^{-1} \text{ min}^{-1}$. As can be inferred from calculation of the constants k , the reaction is of the second order.

13. To study the kinetics of the reaction



a solution was prepared with the following initial concentrations of the components: 0.007574 mole/litre of perchloric acid and 0.12 mole/litre of ethylene oxide. The course of the reaction was monitored dilatometrically (by measuring the volume of the solution as a function of time). At 293 K, the following results were obtained:

t , min	0	30	60	135	300	∞
Dilatometer reading	18.48	18.05	17.62	16.71	15.22	12.29

Determine the order of the reaction with respect to ethylene and its rate constant.

Solution. Assume that the reaction is of the first order:

$$a = 18.48 - 12.29 = 6.19$$

$$a - x = 18.05 - 12.29 = 5.76$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{30} \log \frac{6.19}{5.76} = 2.40 \times 10^{-3} \text{ min}^{-1}$$

$k = 2.40, 2.46, 2.49, 2.49$, the mean value being $2.46 \times 10^{-3} \text{ min}^{-1}$.

Consequently, the reaction is of the first order.

14. The reaction between bromine and ethanol was conducted under the following conditions:

t , min	0	4
c_1 , mole/litre	0.00814	0.00610
c_2 , mole/litre	0.00424	0.00314

Determine the order of the reaction.

Solution. Determine the reaction order according to the equation

$$n = \frac{\log (\Delta c_1 / \Delta t) - \log \Delta c_2 / \Delta t}{\log c_1 - \log c_2}$$

Substitute the corresponding values. Since $\frac{\Delta c}{\Delta t} = \bar{w}$ is the mean reaction rate, c_1 and c_2 must also be expressed in terms of mean values:

$$c_1 = \frac{0.00814 + 0.00610}{2} = 0.00712$$

$$c_2 = \frac{0.00424 + 0.00314}{2} = 0.00369$$

$$n = \frac{\log \frac{0.00814 - 0.00610}{4} - \log \frac{0.00424 - 0.00314}{4}}{\log 0.00712 - \log 0.00369} = 0.91 \approx 1$$

Hence, the reaction is of the first order.

15. Calculate the order of the reaction step determining the rate of pyrolysis of diborane B_2H_6 (g) at 373 K, proceeding from the following system pressure increase rates as a function of diborane concentration:

$c_{B_2H_6} \times 10^2$, mole/litre	2.153	0.433
Pressure increase rate \times 10^4 , mole/litre h	7.4	0.73

Solution. Write the following for an n th-order reaction:

$$-\frac{dc}{dt} = kc^n, \quad \log \left(-\frac{dc}{dt} \right) = \log k + n \log c$$

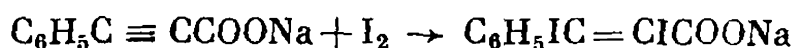
Hence,

$$n = \frac{\log (-dc/dt)_1 - \log (-dc/dt)_2}{\log c_1 - \log c_2}$$

The pressure increase rate is proportional to $\frac{dc}{dt}$. Then

$$n = \frac{\log 7.4 - \log 0.73}{\log 2.153 - \log 0.433} = 1.44 \approx \frac{3}{2}$$

16. Equivalent amounts of iodine and sodium phenylpropylate, $C_6H_5C \equiv CCOONa$, react at 298 K according to the equation



The course of the reaction was monitored by periodic titration of iodine with a sodium hyposulphite solution to determine the decrease in the iodine concentration.

Two runs were conducted with the following results:

	Run 1		Run 2	
Time, s	0	29	0	34.5
Amount of $Na_2S_2O_3$ spent in titration of 250-cm ³ samples, cm ³	24.96	8.32	21.00	7.00

Determine the order of the reaction and its rate constant.

Solution. Since the reaction involved equivalent amounts of the initial substances and the iodine concentration had decreased exactly three-fold by the end of the two runs, the order of this reaction can be determined by the Ostwald-Noyes method:

$$n = \frac{\log(t_2/t_1)}{\log(c'_A/c''_A)} + 1$$

Substitution of numerical values into this equation gives

$$n = \frac{\log(34.5/29)}{\log(24.96 \times 10^{-6}/21.00 \times 10^{-6})} + 1 = \frac{0.0754}{0.0751} + 1 \approx 2$$

Thus, the reaction between iodine and sodium phenylpropylate is of the second order. Calculate the rate constant of this reaction using Eq. (21.20).

For the first run,

$$k_1 = \frac{1}{29} \frac{16.64 \times 10^{-6}}{24.96 \times 10^{-6} \times 8.32 \times 10^{-6}} = 2.763 \times 10^{-3}$$

For the second experiment,

$$k_2 = \frac{1}{34.5} \frac{14 \times 10^{-6}}{21.00 \times 10^{-6} \times 7.00 \times 10^{-6}} = 2.761 \times 10^{-3}$$

The above results corroborate the order of the reaction in view of the complete coincidence of the rate constants.

Problems

1. The concentration of tritium atoms in air is about 5×10^{-15} mole/litre. The half-life of tritium is nearly 12 years. How many years will it take for the dissociation of the tritium present in air to be 90% complete? Ignore the replenishment of tritium in air as a result of synthetic reactions.

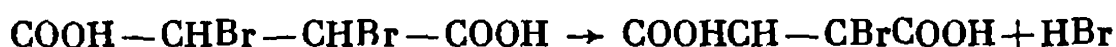
2. A solution (20%) of cane sugar with clockwise rotation of the polarization plane through 34.50° is inverted in 0.5 *N* lactic acid at 298 K. After 1435 min, the rotation of the solution reaches $+31.10^\circ$, after 11 360 min it reaches $+13.98^\circ$, and, finally, after the inversion is complete, the rotation angle becomes -10.77° . The cane sugar solution rotates the polarization plane to the right, and the mixture of inversion products rotates it to the left. In both cases, the rotation angle is proportional to the concentration of the solutes. The reaction is of the first order. Calculate the inversion rate constant and determine the time it will take the inversion of sugar to be 90% complete.

3. The dissociation of hydrogen peroxide in an aqueous solution is $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. The kinetics of this reaction was studied

by titration of samples of equal volumes with potassium permanganate. Determine the order of the reaction by all possible methods and calculate the mean value of its rate constant, proceeding from the following data:

Elapsed time, min	0	5	10	15	20	30	40
Amount of 0.0015M KMnO ₄ spent in tit- ration of 2-cm ³ sam- ples, cm ³	23.6	18.1	14.8	12.1	9.4	5.8	3.7

4. When heated, a solution of dibromo-succinic acid dissociates into bromo-maleic acid and HBr according to the equation



When the solution was titrated with a standard alkali solution, after t min the titre throughout the volume of the solution changed as follows:

t , min	0	214	380
V_{alk} , cm ³	12.11	12.44	12.68

Calculate the rate constant of the reaction. How long will it take for one third of dibromo-succinic acid to dissociate?

5. Determine the order of the reaction $\text{A}_{(\text{g})} \rightarrow \text{B}_{(\text{g})} + \text{C}_{(\text{g})} + \text{D}_{(\text{g})}$ from the pressure changes in the course of the reaction. Calculate the mean reaction rate constant ($V = \text{const}$, 298 K) if

t , min	0	6.5	13.0	19.9
$P \times 10^{-3}$, Pa	41.6	54.5	63.7	74.2

6. A bimolecular reaction with $c_A = c_B$ is 25% complete within 10 min. How long will it take for the reaction to be 50% complete at the same temperature?

7. The rate constant of the recombination of ions H^+ and PhG^- (phenyl glycinate) in an HPhG molecule at 298 K is $k = 10^{11.59} \text{ s}^{-1} \text{ mole}^{-1} \text{ litre}$. Calculate the time period within which the reaction is 99.999% complete if the concentrations of the ions are $[\text{H}^+] = [\text{PhG}^-] = 0.001 \text{ mole/litre}$.

8. The rate of oxidation of butanol with hypochlorous acid is independent of the concentration of the former and proportional to the squared concentration of the latter. Calculate the time it will take for the oxidation of butanol with hypochlorous acid to be 90% complete in a solution containing 0.1 mole/litre HClO and 1 mole/litre of the alcohol at 298.2 K. The reaction rate constant is $24 \text{ min}^{-1} \text{ mole}^{-1} \text{ litre}$ at 298.2 K.

9. The rate constant of the reaction



is $5.4 \text{ min}^{-1} \text{ mole}^{-1} \text{ litre}$. Calculate the percentage of the ester that will react within 10 min if (a) the initial concentrations of the alkali and ester are 0.02 mole/litre and (b) the alkali concentration is 0.02 mole/litre and that of the ester, 0.01 mole/litre.

10. At a given temperature, a 0.01 *N* solution of ethyl acetate is saponified with 0.002 *N* NaOH within 23 min, the degree of saponification being 10%. How many minutes will it take for the acetic ester solution to be saponified to the same degree with 0.005 *N* NaOH if the ester saponification reaction is of the second order and the alkalis dissociate completely?

11. Calculate the rate constant ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$, $\text{litre mole}^{-1} \text{ s}^{-1}$, and $\text{litre mole}^{-1} \text{ min}^{-1}$), if the rate of a second-order reaction is $4.5 \times 10^{-7} \text{ mole cm}^{-3} \text{ s}^{-1}$, the concentration of one reactant being $1.5 \times 10^{-2} \text{ mole/litre}$ and that of the other, $2.5 \times 10^{-3} \text{ mole/litre}$.

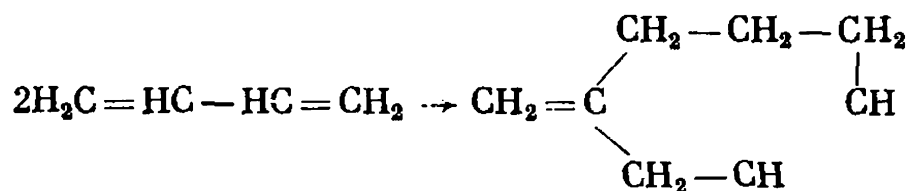
12. The rate of a dissociation reaction ($\text{A} \rightarrow \text{product}$) obeys the second-order equation $-d[\text{A}]/dt = k[\text{A}]^2$. The concentration of substance A varied in the course of time as follows:

$t (\pm 1 \text{ s}), \text{ s}$	0	200	400	600	800
$\text{A} (\pm 1\%), \text{ mg/cm}^3$	16.4	15.0	13.4	12.8	11.5

Calculate, for each pair of points, the rate constant of the second-order reaction and evaluate the accuracy of each calculation. In which case is the accuracy minimum and in which case is it maximum?

13. The reaction of formaldehyde with hydrogen peroxide yields formic acid (second-order reaction): $\text{HCHO} + \text{H}_2\text{O}_2 = \text{HCOOH} + \text{H}_2\text{O}$. If equal volumes of molar solutions of H_2O_2 and HCHO are mixed, two hours later, at 333.2 K, the concentration of formic acid becomes 0.215 mole/litre. Calculate the rate constant of the reaction and determine the time it will take for the reaction to be 90% complete. How much time will it take to achieve the same degree of conversion if the initial solutions of H_2O_2 and HCHO are diluted ten-fold and mixed.

14. The dimerization of butadiene in the gas phase is a second-order reaction with respect to butadiene. The kinetics of this process can be studied by measuring the pressure of the reacting system at definite time intervals with the volume remaining invariable. The following were the results of an experiment with the reaction



at 599.2 K:

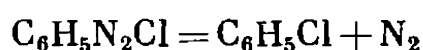
t , min	0	3.25	6.12	10.08	14.30	20.78
$P \times 10^{-3}$, Pa	84.2	82.4	80.9	78.9	76.8	74.2
t , min	29.18	36.38	49.50	60.87	68.05	77.57
$P \times 10^{-3}$, Pa	71.4	69.5	66.4	64.4	63.3	62.0
t , min	90.05	103.58	119.00	135.72		
$P \times 10^{-3}$, Pa	60.4	59.0	57.7	56.4		

Calculate the rate constant graphically and analytically.

15. The oxidation of FeCl_2 with KClO_3 in the presence of HCl is a third-order reaction. If time is given in minutes and the concentration in mole/litre, the rate constant of this reaction approximately equals unity. Calculate the concentration of FeCl_2 one and a half hours after the onset of the reaction if the initial concentrations of all reactants are 0.2 mole/litre.

16. Substance A is mixed in equal amounts with substances B and C, $c_0 = 1$ mole/litre. After 1000 s half of substance A has reacted. Determine the amount of substance A remaining after 2000 s if the reaction is of (a) the first order, (b) the second order, (c) the third order, and (d) the zeroth order. How much of the substance will react within 1000 s in all cases if the reaction rate constant is $k = 1$.

17. Phenyl diazochloride dissociates as follows:



The following results were obtained at 323 K and an initial concentration of 10 g/litre:

Time, min	6	9	12	14	18	22	24	26	30	∞
N_2 yield, cm^3	19.3	26.0	32.6	36.0	41.3	45.0	46.5	48.3	50.4	58.3

Process the above data by the differential and integral methods and determine the order of the reaction and its rate constant.

18. The reaction of ammonia dissociation on a hot tungsten wire proceeds according to the stoichiometric equation $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. The pressure increased as follows at different points in time during the reaction:

Time, s	100	200	400	600	800	1000
Pressure increase, Pa	1466.3	2945.9	5865.2	8837.8	11 717.0	14 663.0

Plot these results and determine the order of the reaction. If the initial pressure was 200 mm Hg, calculate the rate constant (expressing concentrations in terms of pressure in pascals) and indicate its dimension.

19. The kinetics of catalytic dissociation of ammonia into simple substances was studied at 1373 K. The time necessary for dissociation

of half the entire amount of ammonia (nitrogen and hydrogen being absent at first) depends as follows on the initial ammonia pressure:

P , mm Hg	265	130	58
$t_{1/2}$, min	7.6	3.7	1.7

Determine the order of the reaction and its rate constant.

20. Determine the order of the reaction $2\text{CO} = \text{CO}_2 + \text{C}$ at 583.2 K if the pressure decreased within 30 minutes from 1.049×10^5 to 0.924×10^5 Pa, then, within the same time interval, from 0.714×10^5 to 0.624×10^5 Pa ($V = \text{const}$).

21. The total pressure of the system decreased as follows during the reaction between equivalent amounts of carbon monoxide and chlorine according to the equation $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ at 300 K in the presence of a catalyst:

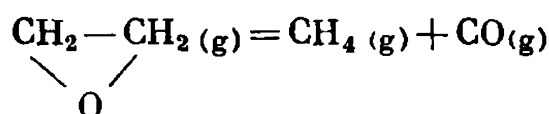
t , min	0	5	10	15	21
$P \times 10^{-5}$, Pa	0.965	0.900	0.829	0.779	0.735

Determine the order of the reaction ($V = \text{const}$).

22. Determine the order of the reaction in which *para*-hydrogen is converted into *ortho*-hydrogen at 923 K, proceeding from the following relationships between the half-time of conversion and pressure:

$P \times 10^{-5}$, Pa	0.067	0.133	0.267	0.533
$t_{1/2}$, s	648	450	318	222

23. Determine the order of the ethylene oxide dissociation reaction



and calculate the rate constant ($V = \text{const}$) if the total pressure of the reaction mixture at 687.7 K varies as follows in the course of time:

t , min	0	4	7	9	12	18
$P \times 10^{-5}$, Pa	0.155	0.163	0.168	0.172	0.178	0.188

24. The following data have been obtained for the rate of inversion of cane sugar in the presence of hydrochloric acid:

Time, s	0	1035	3113	4857	9231	12 834	18 520	26 320	32 640	76 969	∞
Rotation angle, α , deg	11.20	10.35	8.87	7.64	5.19	3.61	1.60	-0.16	-1.10	-3.26	-3.37

Determine the order and rate constant of the reaction.

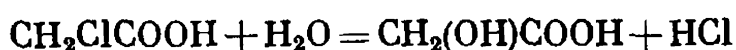
25. At 583.2 K, $\text{AsH}_3(\text{g})$ dissociates into solid arsenic and gaseous hydrogen. The pressure varied as follows during the reaction (the

arsenic vapour pressure is ignored):

$t, \text{ h}$	0	5.5	6.5	8
$P \times 10^{-5}, \text{ Pa}$	0.978	1.074	1.091	1.114

Determine the order of the $\text{AsH}_{3(g)}$ dissociation reaction and calculate its rate constant ($V = \text{const}$).

26. Monochloroacetic acid reacts with water (present in excess amount) at 298 K as follows:

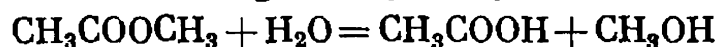


The course of the reaction was monitored by taking samples which were titrated with an alkali. The results of titration of the samples of equal size with an alkali solution are as follows:

Time, min	0	600	780	2070
Amount of alkali, cm^3	12.9	15.8	16.4	20.5

Determine the order of the reaction, calculate its rate constant and the time necessary for all three acids to be present in equivalent amounts.

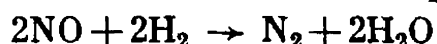
27. Methyl acetate undergoes hydrolysis:



The kinetics of this reaction was studied by titration of samples of the reaction mixture, taken in equal amounts, with an alkali. Determine the order of the reaction by all possible methods and calculate the mean value of its rate constant, proceeding from the following data:

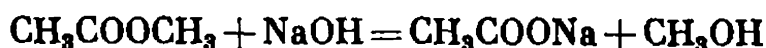
Elapsed time, min	0	30	60	90	120	150
Amount of 0.05 <i>N</i> alkali solution spent in titration of 2- cm^3 sample, cm^3	12.70	13.81	16.73	15.52	16.80	20.22

28. The reduction of nitrogen(II) oxide with hydrogen at 298 K proceeds according to the stoichiometric equation



If the initial gases are taken in equivalent amounts at $0.454 \times 10^5 \text{ Pa}$, their pressure is reduced by one half within 102 s, and if the initial pressure was $0.384 \times 10^5 \text{ Pa}$, it becomes half as high within 140 s. Determine the order of the reaction ($V = \text{const}$) proceeding from the relationship between the half-life of the initial substance and the initial concentration.

29. Methyl acetate is saponified with an alkali at 298 K in the reaction

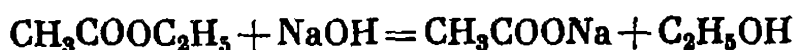


The following are the results of studying this reaction:

$t, \text{ min}$	3	5	7	10	15	25
$c_{\text{NaOH}}, \text{ g-equiv/litre}$	0.00740	0.00634	0.00550	0.00464	0.00363	0.00254

The initial concentrations of the alkali and ester are the same and equal to 0.01 g-equiv/litre. Determine the order of ester saponification reaction and calculate the mean value of its rate constant.

30. Ethyl acetate is saponified with an alkali at 298 K by the reaction



The kinetics of this reaction was studied by titration of equally sized samples of the mixture with an acid. Determine the order of the reaction by all possible methods and calculate the mean value of its rate constant, proceeding from the data:

Time, min	0	4.9	10.4	28.2	∞
Amount of 0.01 N HCl spent in titration of 0.1-cm ³ sample, cm ³	61.95	50.59	42.40	29.35	14.9

31. As the initial concentration increases from 0.502 to 1.007 mole/litre in a reaction, the half-life decreases from 51 to 26 s. Calculate the order of this reaction and its rate constant.

32. Nitrogen pentoxide dissociates as follows: $\text{N}_2\text{O}_5 \rightarrow 0.5\text{O}_2 + \text{N}_2\text{O}_4$. The kinetics of this process was studied by measuring the pressure of the reacting system at definite time intervals ($V = \text{const}$) with the following results at 328.1 K:

Time, min	3	4	5	6	7	8	9	10	12
Pressure increase $\times 10^{-3}$, Pa	8.7	12.7	15.5	18.1	20.1	22.4	24.4	26.3	29.1
Time, min	14	16	18	22	26	30	38		
Pressure increase $\times 10^{-3}$, Pa	31.4	33.6	35.5	38.5	39.9	41.2	42.6		

Calculate the order of this reaction, the mean value of its rate constant, and the half-life of nitrogen pentoxide.

33. The rate constant of a reaction whose order is $3/2$ at 303 K is $3.0 \times 10^{-5} \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ s}^{-1}$. Determine the rate constant in (a) $(\text{cm}^3)^{1/2} \text{ mole}^{1/2} \text{ min}^{-1}$ and (b) $(\text{cm}^3)^{1/2} \text{ molecule}^{1/2} \text{ s}^{-1}$. Calculate the initial rate at which the substance is spent and its half-life (s) for the initial concentration $c_0 = 0.042 \text{ mole/litre}$ of this substance. Determine the time it takes for the reactant concentration to reach 0.002 mole/litre.

34. The order of the reaction in which a gas dissociates is $3/2$. At the beginning of the experiment, the gas concentration was $5.2 \times 10^{-4} \text{ mole/litre}$. What will be the dimensions of the rate constant if the dissociation of the gas is 55% complete within 50 min?

Multivariant Problem

Determine the order and rate constant of a reaction at temperature T , K, proceeding from the following data on the course of the process from moment t onward:

Variant	Reaction	Time, min	Reaction parameter	T, K
1	$2\text{NCl}_3 (\text{liq}) \rightarrow \text{N}_2 + 3\text{Cl}_2$ a — volume of $\text{N}_2 \times 10^{-6}$, m^3 ; Cl_2 is absorbed		a	298.2
		4	10	
		6	13	
		22	26	
		∞	28.5	
2	$2\text{HgCl}_2 + \text{HCOONa} \rightarrow \text{Hg}_2\text{Cl}_2 + \text{NaCl} + \text{HCl} + \text{CO}_2$ a — HgCl_2 concentration, mole/litre, b — HCOONa concentration, mole/litre		a b	298.2
		0	0.1034 0.1734	
		3	0.0679 —	
		0	0.0503 0.1734	
		3	0.0326	
		0	0.1028 1.0227	
		1	— 0.9579	
		0	0.1028 0.3790	
3	$\text{C}_6\text{H}_5\text{C} \equiv \text{CCOONa} + \text{I}_2 \rightarrow \text{C}_6\text{H}_5\text{IC} = \text{CICOONa}$ The initial concentrations are equivalent: a — amount of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ spent in the titration of a 25×10^{-7} - m^3 sample, cm^3		a	298.2
		0	24.29	
		29	8.32	
		0	21	
		34.5	7	
4	$\text{Ru} \rightarrow \text{RaA}$ a — volume of gaseous $\text{Ra} \times 10^{-6}$, m^3		a	293.2
		0	0.102	
		70	0.062	
		110	0.044	
		140	0.033	
		165	0.025	
		200	0.019	
		250	0.016	
		360	0.007	
		450	0.003	
		600	0.002	
		750	0.000	
5	$2\text{C}_2\text{H}_5\text{OH} + 2\text{Br}_2 \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + 4\text{HBr}$ The alcohol is taken in a large amount. a — bromine concentration $\times 10^3$, mole/litre		a	298.2
		0	4.24	
		4	3.14	
		6	2.49	
		10	2.24	
		15	1.78	
		0	8.14	
		4	6.10	

(Table continued)

Vari- ant	Reaction	Time, min	Reaction parameter	T, K
6	$2\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}_2\text{O}$ In an aqueous solution: a —amount of KMnO_4 spent in the titration of a sample $\times 10^{-6}$, m^3	10	4.45	303.2
		15	3.73	
			a	
		0	23.89	
		11.5	19.30	
		27.1	14.50	
7	$\text{K}_2\text{S}_2\text{O}_8 + 2\text{KI} \rightarrow 2\text{K}_2\text{SO}_4 + \text{I}_2$ a —amount of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ spent in the titration of a 25 $\times 10^{-6}$ - m^3 sample, cm^3	42.5	10.95	298.2
			a	
		9	4.52	
		16	7.80	
		32	14.19	
8	A N_2O_5 solution in CCl_4 dissociates releasing O_2 a — O_2 volume, cm^3	∞	20.05	313.2
			a	
		20	11.4	
		40	19.9	
		60	23.9	
		80	27.2	
		100	29.5	
9	H_2O_2 dissociates in the presence of colloidal platinum, releasing O_2 a — O_2 volume, cm^3	∞	34.75	303.2
			a	
		10	3.3	
		30	8.1	
10	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} = \text{CH}_3\text{COONa}$ $+ \text{C}_2\text{H}_5\text{OH}$ a and b —initial concentrations of $\text{CH}_3\text{COOC}_2\text{H}_5$ and NaOH , mole/litre; x —decrease in the amount of initial substances, mole/litre	∞	15.6	291.2
			$a - x$ $b - x$	
		0	0.00980 0.00486	
		178	0.00892 0.00398	
		273	0.00864 0.00370	
		531	0.00792 0.00297	
		866	0.00724 0.00230	
		1510	0.00646 0.00151	
		1918	0.00603 0.00109	
		2401	0.00574 0.00080	
11	$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ c —current sugar concentration, mole/litre; c_0 —initial sugar concentration, 0.65 mole/litre		c_0/c	298.2
		0	1	
		1435	1.081	
		4315	1.266	
		7070	1.464	
		11360	1.830	

(Table concluded)

Vari- ant	Reaction	Time, min	Reaction parameter	T, K
12	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} = \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$ $a = b$ — initial $\text{CH}_3\text{COOC}_2\text{H}_5$ and NaOH concentrations, mole/litre; x — decrease in the initial substance concentrations, mole/litre	14170	2.117	293.7
		16935	2.466	
		19815	2.857	
		29925	4.962	
			$a - x$	
		0	0.0200	
		300	0.0128	
		900	0.00766	
		1380	0.00540	
		2100	0.00426	
		3300	0.00289	
		7200	0.00138	
13	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$ a — N_2O_5 concentration, mole/litre		a	298.2
		0	2.33	
		184	2.08	
		319	1.91	
		526	1.67	
		867	1.36	
		1198	1.11	
		1877	0.72	
		2315	0.55	
		3144	0.34	

CHAPTER 22
Composite Reactions

Basic Equations and Symbols

In the case of monomolecular reversible reactions of the $A \overset{k_1}{\rightleftharpoons} B$ type, the differential forms of the kinetic equation are

$$\frac{dx}{dt} = k_1 ([A]_0 - x) - k_2 ([B]_0 + x) \tag{22.1}$$

and

$$\frac{dA}{dt} = -k_1 [A] + k_2 [B] \tag{22.2}$$

At the equilibrium $\frac{d[A]}{dt} = 0$ and if $[B] = 0$ at $t = 0$,

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_2} = K \quad (22.3)$$

$$[B]_{\text{eq}} = [A]_0 - [A]_{\text{eq}} \quad (22.4)$$

$$[A]_{\text{eq}} = \frac{k_2}{k_1 + k_2} [A]_0 \quad (22.5)$$

where $[A]$ and $[B]$ are the current concentrations of substances A and B, $[A]_0$ is the concentration of A at $t = 0$, k_1 and k_2 are the rate constants of the forward and backward reactions, $[A]_{\text{eq}}$ and $[B]_{\text{eq}}$ are the concentrations of A and B in the state of equilibrium, and K is the equilibrium constant.

The integral forms of the kinetic equation are

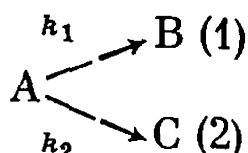
$$k_1 + k_2 = \frac{2.3}{t} \log \frac{k_1 [A]_0 - k_2 [B]_0}{k_1 ([A]_0 - x) - k_2 ([B]_0 + x)} \quad (22.6)$$

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{k_1 [A]_0 - k_2 [B]_0}{k_1 [A] - k_2 [B]} \quad (22.6a)$$

If $[B]_0 = 0$ at $t = 0$,

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{[A]_0 - [A]_{\text{eq}}}{[A] - [A]_{\text{eq}}} \quad (22.7)$$

For monomolecular parallel reactions of the



type, the differential forms of the kinetic equation are

$$\frac{dx}{dt} = (k_1 + k_2) ([A]_0 - x) \quad (22.8)$$

$$-\frac{d[A]}{dt} = (k_1 + k_2) [A] \quad (22.9)$$

The integral forms of the kinetic equation are

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{[A]_0}{[A]_0 - x} \quad (22.10)$$

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{[A]_0}{[A]} \quad (22.11)$$

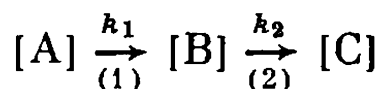
where k_1 and k_2 are the rate constants of the first and second reactions. The rate constants of individual steps of reactions of the above type are determined from the relation

$$x_1/x_2 = k_1/k_2 \quad (22.12)$$

where x_1 and x_2 stand for the numbers of moles of substances B and C formed by instant t or the increase in the concentrations of these substances. The current concentration of the initial substance is

$$[A] = [A]_0 - x$$

For monomolecular consecutive reactions of the



type, the differential forms of the kinetic equation are

$$\frac{dx}{dt} = k_1 ([A]_0 - x) \quad (22.13)$$

$$\frac{d(x-y)}{dt} = k_1 ([A]_0 - x) - k_2 (x-y) \quad (22.14)$$

$$-\frac{d[A]}{dt} = -k_1 [A] \quad (22.15)$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] \quad (22.16)$$

$$\frac{dc}{dt} = k_2 [B] \quad (22.17)$$

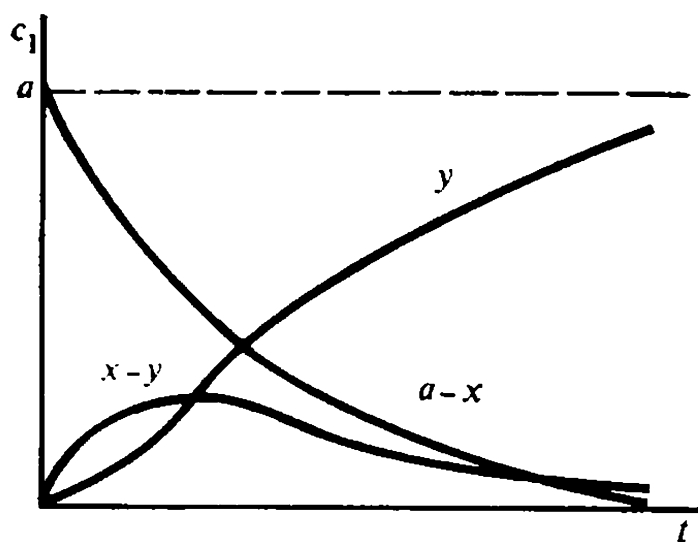


Fig. 42. Concentrations of initial substance A, intermediate B, and reaction product C versus duration of the consecutive first-order reaction

The integral forms of the kinetic equation are

$$[A]_0 - x = [A]_0 e^{-k_1 t} \quad (22.18)$$

$$x - y = [A]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (22.19)$$

$$y = [A]_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \quad (22.20)$$

$$[A] = [A]_0 e^{-k_1 t} \quad (22.21)$$

$$[B] = \frac{k_2 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (22.22)$$

$$[C] = [A]_0 - [A] - [B] \quad (22.23)$$

where $[A]$, $[B]$, and $[C]$ are the current concentrations of substances A, B, and C; $[A]_0$ is the concentration of substance A at $t = 0$; k_1 and k_2 are the rate constants of the first and second reactions: $[A] = ([A]_0 - x)$; $[B] = x - y$; $[C] = y$.

Corresponding to the maximum on the $[B] = f(t)$ curve (Fig. 42) are the equations

$$\left(\frac{d[B]}{dt} \right)_{\max} = 0 \quad (22.24)$$

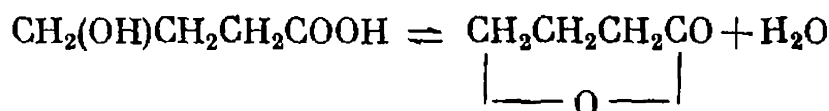
$$\frac{[B]_{\max}}{[A]_{\max}} = \frac{k_1}{k_2} \quad (22.25)$$

$$t_{\max} = \frac{2.3 (\log k_1 - \log k_2)}{k_1 - k_2} \quad (22.26)$$

in which t_{\max} is the time corresponding to the maximum concentration of substance B.

Exercises

1. γ -Hydroxybutyric acid dissociates into lactone and water in an aqueous solution at 293 K, in the presence of acids (such as HCl), according to the equation



A 0.176 *N* solution of γ -hydroxybutyric acid was prepared. At the beginning of the experiment, 18.23 cm³ of 0.1 *N* Ba(OH)₂ was used per 10 cm³ of the acid during titration with phenolphthalein, after 21 minutes 15.84 cm³ of barium hydrate was used for the same amount of the acid, and after 45 hours, 4.95 cm³. The latter amount of barium hydrate remains the same throughout the subsequent repeated titration. How much time must elapse since the beginning of the experiment for 6.67 cm³ of barium hydrate to be spent in the titration of the acid?

Solution. Denote the initial concentration of the acid by a , the initial concentration of lactone by a' , and the amount of lactone formed within the time interval t by x . Then,

$$\frac{dx}{dt} = k_1 (a - x) - k_2 (a' - x)$$

where k_1 and k_2 are the reaction rate constants;

$$\frac{dx}{(k_1 a - k_2 a') - (k_1 + k_2) x} = dt$$

$$-\frac{1}{k_1 + k_2} \ln [(k_1 a - k_2 a') - (k_1 + k_2) x] = t + \text{const}$$

At the onset of the reaction, $t = 0$ and $x = 0$, hence,

$$\begin{aligned} \text{const} &= -\frac{1}{k_1 - k_2} \ln (k_1 a - k_2 a') \\ (k_1 + k_2) &= \frac{1}{t} \ln \frac{k_1 a - k_2 a'}{(k_1 a - k_2 a') - (k_1 + k_2) x} \end{aligned} \quad (1)$$

Multiplication of the numerator and denominator of Eq. (1) by k_2 , transformation of \ln into \log , and substitution of the equilibrium constant K_c for k_1/k_2 give

$$\frac{k_1 + k_2}{2.303} = \frac{1}{t} \log \frac{K_c a - a'}{(K_c a - a') - (1 + K_c) x}$$

The quantity $(k_1 + k_2)/2.303$ must be constant at a given temperature throughout the reaction. Since $a' = 0$,

$$\frac{k_1 + k_2}{2.303} = \frac{1}{t} \log \frac{K_c a}{K_c a - (1 + K_c) x} \quad (2)$$

Express the initial concentration a of the acid in cubic centimetres of the barium hydroxide solution. Then $a = 18.23 \text{ cm}^3$; the amount of the lactone x formed within $t = 21 \text{ min}$, also expressed in cubic centimetres of the barium hydroxide solution, will be $x = 18.23 - 15.84 = 2.39 \text{ cm}^3$.

In order to calculate $\frac{k_1 + k_2}{2.303}$, determine the equilibrium constant

$K_c = \frac{c_{\text{lactone}}}{c_{\gamma\text{-hydroxybutyric acid}}}$. Determine the concentration of lactone from the difference between the amounts of barium hydroxide solution spent in the titration of γ -hydroxybutyric acid at the beginning of the reaction and after equilibrium is reached. Determine the concentration of γ -hydroxybutyric acid from the amount of barium hydroxide solution spent in the titration of the same quantity of the solution upon reaching equilibrium. Consequently,

$$K_c = \frac{(18.23 - 4.95)}{4.95} = \frac{13.28}{4.95} = 2.68$$

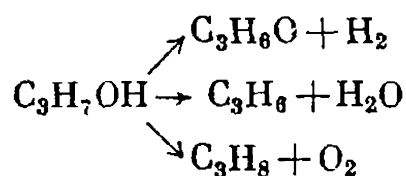
Substitution of the values of K_c , t , a , and x into Eq. (2) gives

$$\frac{k_1 + k_2}{2.303} = \frac{1}{21} \log \frac{2.68 \times 18.23}{2.68 \times 18.23 - (1 + 2.68) 2.39} = 0.0041$$

K_c and a remain invariable throughout the reaction, while x changes: $x = 18.23 - 6.67 = 11.56$ and, consequently,

$$t = \frac{1}{0.0041} \log \frac{2.68 \times 18.23}{2.68 \times 18.23 - (1 + 2.68) 11.56} = 217 \text{ min}$$

2. The reaction of dissociation of isopropanol in the presence of the vanadium trioxide catalyst at 588 K is



The concentrations of the substances involved in the reaction, measured at 4.3 s intervals after the experiment began, are as follows (mmoles): $c_{\text{C}_3\text{H}_7\text{OH}} = 27.4$, $c_{\text{C}_3\text{H}_6\text{O}} = 7.5$, $c_{\text{C}_3\text{H}_8} = 8.1$, and $c_{\text{C}_3\text{H}_8} = 1.7$. Determine the rate constant of each reaction if only $\text{C}_3\text{H}_7\text{OH}$ was present initially in the system.

Solution. Determine the initial quantity of $\text{C}_3\text{H}_7\text{OH}$:

$$\begin{aligned} [\text{A}]_0 &= c_1 + c_2 + c_3 + c_4 = 27.4 + 7.5 + 8.1 + 1.7 \\ &= 44.7 \text{ mmole/litre} \end{aligned}$$

Calculate the sum of the reaction rate constants:

$$\begin{aligned} \frac{dx}{dt} &= \frac{dx_1}{dt} + \frac{dx_2}{dt} + \frac{dx_3}{dt} \\ w = \frac{dx}{dt} &= k_1 ([\text{A}]_0 - x) + k_2 ([\text{A}]_0 - x) + k_3 ([\text{A}]_0 - x) \\ &= (k_1 + k_2 + k_3) ([\text{A}]_0 - x) \\ (k_1 + k_2 + k_3) &= \frac{1}{t} \ln \frac{[\text{A}]_0}{[\text{A}]_0 - x} \\ \sum k &= \frac{2.3}{4.3} \log \frac{44.7}{27.4} = 0.115 \text{ s}^{-1} \end{aligned}$$

Determine the rate constant (s^{-1}) of each reaction:

$$\begin{aligned} \frac{dx_1}{dt} &= k_1 ([\text{A}]_0 - x), \quad \frac{x_1}{x_2} = \frac{k_1}{k_2} \\ \frac{dx_2}{dt} &= k_2 ([\text{A}]_0 - x), \quad \frac{x_2}{x_3} = \frac{k_2}{k_3} \\ \frac{dx_3}{dt} &= k_3 ([\text{A}]_0 - x), \quad k_1 = \sum k - (k_2 + k_3) \\ \frac{x_1}{x_2} &= \frac{\sum k - (k_2 + k_3)}{k_2}, \quad \frac{7.5}{8.1} = \frac{0.115 - (k_2 + k_3)}{k_2} \\ 7.5k_2 &= 0.935 - 8.1k_2 - 8.1k_3 \\ 15.6k_2 &= 0.935 - 8.1k_3, \quad k_2 = \frac{0.935 - 8.1k_3}{15.6} \end{aligned}$$

Since $x_2/x_3 = k_2/k_3$, then

$$\frac{8.1}{1.7} = \frac{0.935 - 8.1k_3}{15.6k_3}$$

$$74.3k_3 = 0.935 - 8.1k_3, \quad 82.4k_3 = 0.935, \quad k_3 = 1.135 \times 10^{-2}$$

$$k_2 = \frac{0.935 - 0.01135 \times 8.1}{15.6} = \frac{0.935 - 0.092}{15.6} = \frac{0.843}{15.6} = 5.42 \times 10^{-2} \text{ s}^{-1}$$

$$k_1 = 0.115 - 1.135 \times 10^{-2} - 5.42 \times 10^{-2} = 4.95 \times 10^{-2} \text{ s}^{-1}$$

3. A consecutive first-order reaction proceeds as follows:



At 298 K, the specific rates of the reaction are $k_1 = 0.1 \text{ h}^{-1}$ and $k_2 = 0.05 \text{ h}^{-1}$, the initial concentration of A being $[A]_0 = 1 \text{ mole/litre}$. Calculate (a) the coordinates of the maximum on the $[P] = f(t)$ curve, (b) the time it takes for the concentration of A to become $[A] \leq 0.001 \text{ mole/litre}$ and the duration t_A of the reaction $A \rightarrow P$, (c) the concentrations $[P]$ and $[B]$ at the instant the reaction $A \rightarrow P$ is complete, (d) the time it takes for the concentration of B to become equal to 0.01 mole/litre and the duration of the induction period t_{ind} , (e) the coordinates of the inflection point on the $[B] = f(t)$ curve and (f) the point of intersection of the $[A] = f(t)$ and $[P] = f(t)$ curves. Use the results to plot $[B] = f(t)$.

Solution. Calculate the time at which the concentration of the intermediate product will be maximum:

$$t_{\text{max}} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} = \frac{2.303 - 2.997}{-0.05} = 13.86 \text{ h}$$

Denote the concentration of A at t_{max} by $[A]_{\text{max}}$. Then,

$$[A]_{\text{max}} = [A]_0 e^{-k_1 t} = e^{-0.1 \times 13.86} = 0.249 \text{ mole/litre}$$

and the maximum concentration of the intermediate product will be

$$[P]_{\text{max}} = (k_1/k_2) [A]_{\text{max}} = (0.1/0.05) 0.249 = 0.498 \text{ mole/litre}$$

Assume that $[A]_0 = 0.001 \text{ mole/litre}$, then $0.001 = [A]_0 e^{-k_1 t_A}$;

$$0.001 = e^{-0.1 t_A}; \quad t_A = 69 \text{ h}$$

Calculate the concentration of P at $t = 69 \text{ h}$:

$$[P] = \frac{[A]_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$[P] = \frac{0.1}{0.1 - 0.05} (e^{-0.1 \times 69} - e^{-0.05 \times 69}) = 0.061 \text{ mole/litre}$$

Calculate the concentration of [B] after 69 hours:

$$[B] = [A]_0 - [P] - [A] = 1 - 0.061 - 0.001 = 0.938$$

mole/litre

Calculate the time t_{ind} within which the concentration of [B] becomes 0.01 mole/litre, using the equation

$$\begin{aligned}
 [\text{B}] &= [\text{A}]_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t_{\text{ind}}} - k_1 e^{-k_2 t_{\text{ind}}}) \right] \\
 [\text{B}] &= 1 - \frac{1}{0.05} (0.05 e^{-0.1 t_{\text{ind}}} - 0.1 e^{-0.05 t_{\text{ind}}}) \\
 0.990 \times 0.05 &= 0.05 e^{-0.1 t_{\text{ind}}} - 0.1 e^{-0.05 t_{\text{ind}}} \quad (1)
 \end{aligned}$$

Solve Eq. (1) with respect to t_{ind} by the selection method:

t_{ind} , h	1	2	2.5	3	4
[B], mole/litre	0.000	0.008	0.014	0.018	0.032

Assume that $t_{\text{ind}} = 2$ h. To find the inflection of the $[\text{B}] = f(t)$ curve use the condition $\frac{\partial^2 [\text{B}]}{\partial t^2} = 0$. Differentiation and transformation of the equation

$$[\text{B}] = [\text{A}]_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad (2)$$

give the following expression for the point of inflection:

$$k_1 e^{-k_1 t_{\text{infl}}} - k_2 e^{-k_2 t_{\text{infl}}} = 0 \quad \text{or} \quad 2e^{-0.1 t_{\text{infl}}} - e^{-0.05 t_{\text{infl}}} = 0$$

where t_{infl} is the coordinate of the inflection point, which is found by the method of selection of induction period values: $t_{\text{ind}} = 5, 15, 10, 20$ h. Plot $x = f(t)$

$$x = 2e^{-0.1t} - e^{-0.05t}, \text{ hence, } x = 0.00 \text{ at } t = 13.6 \text{ h}$$

Find the concentration [B] at the inflection point using Eq. (2): [B] = 0.243 mole/litre.

Problems

1. The conversion of ammonium thiocyanide NH_4CNS into thiourea $(\text{NH}_2)_2\text{CS}$ is a reversible monomolecular reaction. Calculate the rate constants of the forward and backward reactions, proceeding from the following data:

Time, min	0	19	38	48	60
Amount of reacted NH_4CNS , %	2.0	6.9	10.4	12.3	13.6

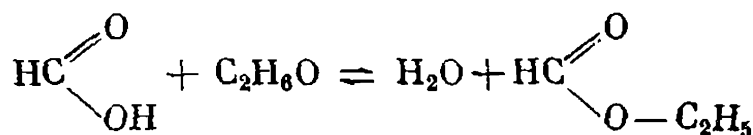
Once the state of equilibrium was reached, the concentration of thiourea became 23.2%.

2. During mixing a solution contained 73.2% ethanol, 0.677 mole HCOOH, and 0.0261% HCl (water is disregarded). To study the formate formation reaction at 298 K, 5-ml samples were taken at different points in time for titration with Ba(OH)₂ with the following results:

<i>t</i> , min	0	50	100	160	290	∞
<i>V</i> , ml	43.52	40.40	37.75	35.10	31.09	24.28

Calculate the constants of formation (*k*₁) and dissociation (*k*₂) of ethyl formate in this solution as well as the equilibrium constant *K* of the reversible reaction if the concentrations of water, ethanol, and hydrogen ions are constant.

3. Ethyl formate forms at 303 K in the following first-order reaction

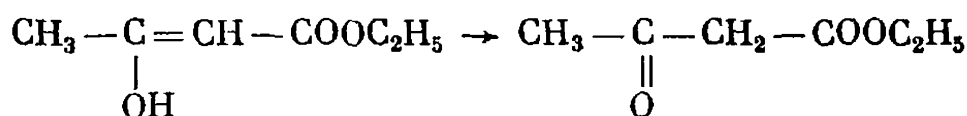


The experimental results are as follows:

Time, min	0	1700	1000	14 000	20 000	40 000
Current acid concentration, cm ³	29.44	28.59	24.77	23.05	21.28	16.80

The acid concentration was determined by titration. The rate constant of the backward reaction is *k*₂ = 1.15 × 10⁻⁵ min⁻¹. The initial concentration of the forward reaction product is 0. Determine the rate constant of the forward reaction.

4. The reaction

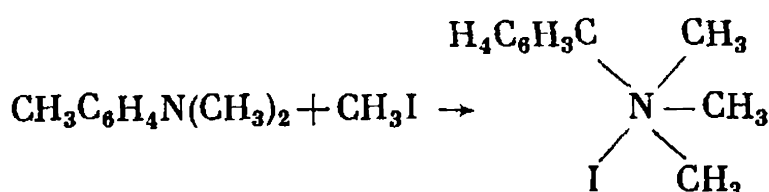


proceeds at 300 K with the following parameters:

Time, min	0	4.25	6.50	9.17	12.0	14.17
Refractive index of the system	1.4450	1.4440	1.4430	1.4420	1.4410	1.4400
Enol form, %	88	84	80	76.3	72.5	69
Time, min	17.5	20.83	24.25	27.5	31.5	∞
Refractive index of the system	1.4390	1.4380	1.4370	1.4360	1.4350	1.4230
Enol form, %	65	61	57	53	49	2

Demonstrate that the conversion of the enol form into the ketone one is a reversible monomolecular reaction. Calculate the rate constants of the forward and backward reactions.

5. The reaction between methyl iodide and a solution of dimethyl *para*-toluidine in nitrobenzene,

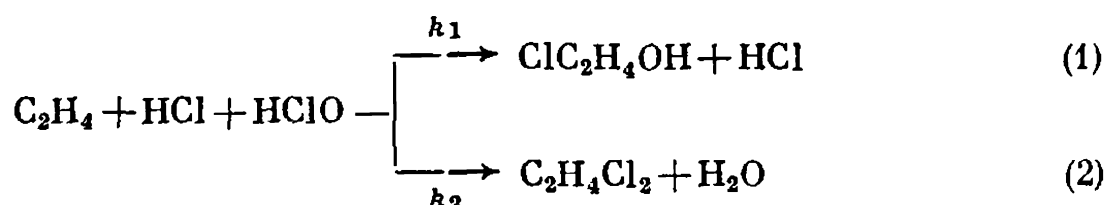


is characterized by the following parameters:

$t, \text{ min}$	10.2	26.5	36.0	78.0
x/c_0	0.175	0.343	0.402	0.523

The equilibrium constant of the reaction is 69.8. The initial concentrations of both reactants are 0.05 mole/litre, and the reaction product is abstracted in the course of the reaction. Determine the type of kinetic equation to be used to describe the kinetic curve and calculate the rate constant of the reaction.

6. The reactions



proceed simultaneously at temperature T . Calculate the rate constant of each reaction if $k_2/k_1 = 0.0314$ and the concentrations (mole/litre) measured in one of the experiments over a period of 240 min are as follows:

	beginning end of experiment	
$[\text{HClO}] \times 10^3, \text{ mole/litre}$	8.675	3.695
$[\text{HCl}] \times 10^3, \text{ mole/litre}$	0.612	0.532

Ethylene is taken in an excess amount.

7. Thermal cracking of crude oil is a consecutive reaction, the intermediate product being petrol which dissociates into gaseous substances. Determine the maximum concentration of petrol and the time it takes to attain this concentration during cracking of

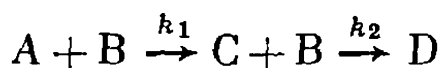
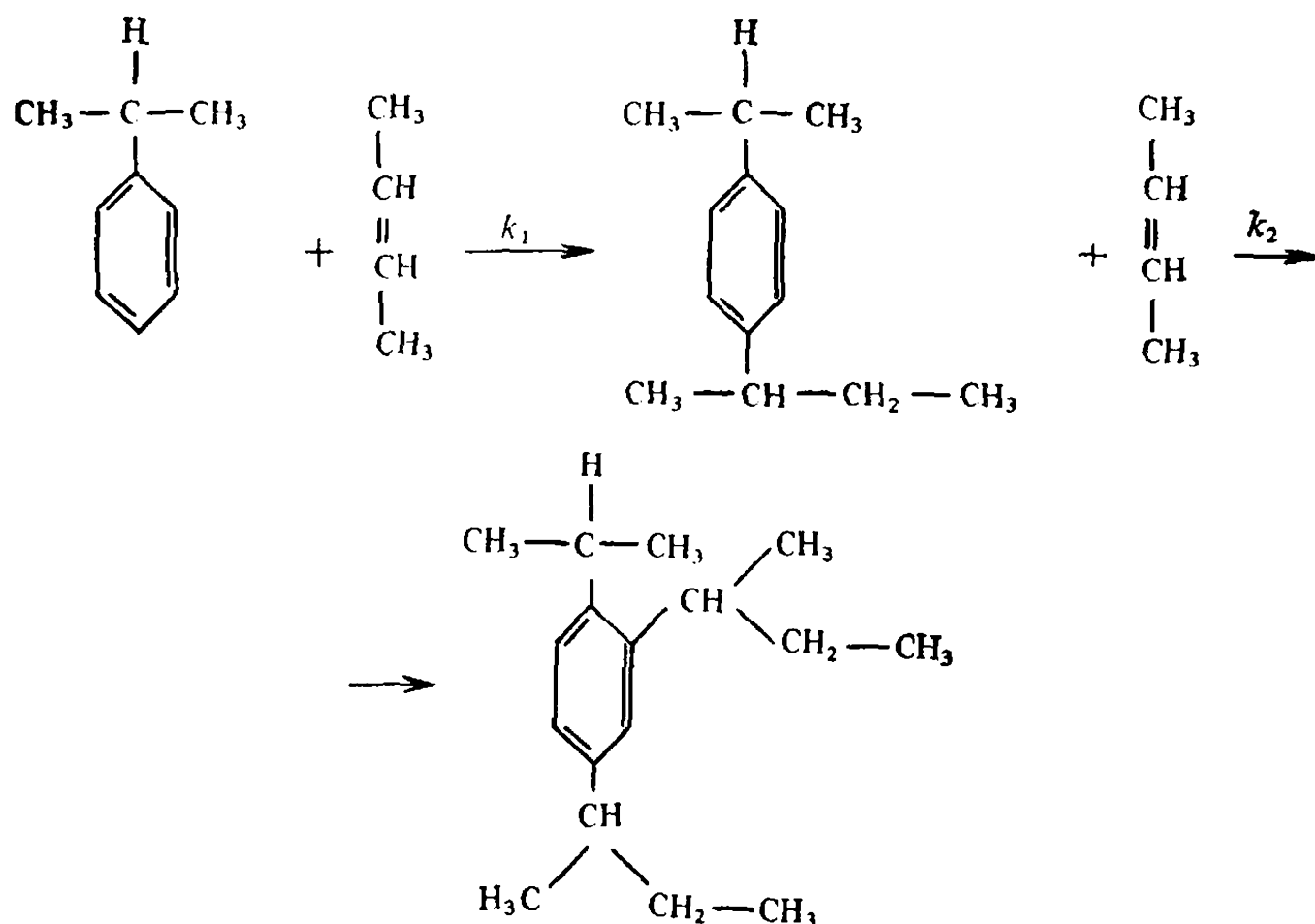
1 tonne of oil if the petrol formation rate constant at 673 K is $k_1 \approx 0.283 \text{ h}^{-1}$ and that of petrol dissociation is $k_2 = 0.102 \text{ h}^{-1}$.

8. Demonstrate that for the reactions



the time of formation of half the amount of B (with respect to the amount at $t = \infty$) and that of formation of half the amount of C are the same although the rate constants k_1 and k_2 are different.

9. The alkylation of isopropyl benzene with *n*-butylene in the presence of HF proceeds as follows:



where A is isopropyl benzene, B is *n*-butylene, C is isopropyl-sec-butylene, and D is the end product. The ratio between the rates of formation of the intermediate and end products is 1.665. The current weight percentage of the mixture components is: A 11.7, C 68.6. Determine the k_1/k_2 ratio.

10. Determine the half-lives of $\text{RaB}(\text{Pb}^*)$ and $\text{RaC}(\text{Bi}^*)$ inter-linked in the genetic series

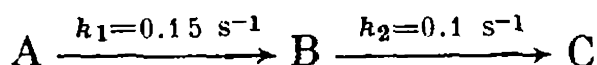


if the concentration of the radioactive nuclei of RaB varies as follows in the course of time:

Number of nuclei, N_{RaB}	100	70	50	34	17	5	4	2.5
τ , min	0	10	20	40	50	80	90	100

and the instant at which the concentrations of accumulated RaC and RaC' are maximum is $\tau_{\text{max}} = 35$ min. (The experiment was carried out with pure RaB nuclei.)

11. Plot the concentrations of A, B, and C versus time for the consecutive first-order reactions



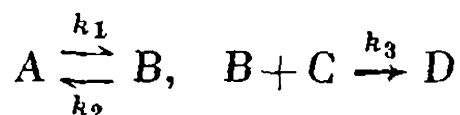
12. The reaction $2A + B \rightarrow 2D$ involves formation of the intermediate substance C in the process



The two reactions are of mixed second order. Write the equation for substance C as a function of substance B (express the concentration of substance C in terms of that of B), proceeding from the boundary conditions $c = 0$ at $t = 0$, and the equation for $d[B]/dt$, which must include the concentrations $[A]_0$, $[B]$, $[B]_0$, and constants k_1 and k_2 .

13. Calculate the steady concentration of substance C for the reaction $2A + B \rightarrow D$, comprising the steps $2A + B \rightarrow C$ and $C + A \rightarrow D$. Will this concentration coincide with the maximum concentration of substance C? Calculate the amount of substance B spent by the time the concentration of substance C reaches 95% of the steady one if $[A]_0 = [B]_0$, $t = 0$, and $k_2 = 25k_1$. What will be the amount of substance D formed by that time? Determine the time period during which the yield of substance C will constitute 95% of its steady concentration if $[A]_0 = 0.02$ mole/litre and $k_1 = 3.0 \times 10^{-4}$ mole/s.

14. Derive the kinetic equations for the reaction



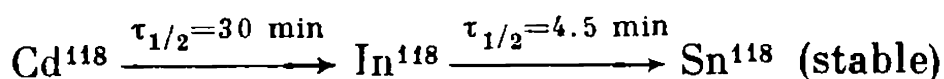
Demonstrate that at high pressures the reaction may be of the first order and that at low pressures it may be of the second order.

15. A sealed vessel having a capacity of 1 cm^3 contains 1 g of radium. Determine the radon pressure at 0°C when the secular equilibrium is reached.

16. Radon decays into RaA which undergoes α -decay. Calculate the time period t_{max} by the end of which the accumulated amount of

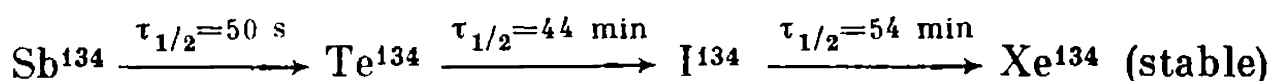
RaA is maximum if pure radon was taken initially. Calculate the maximum amount (g) of RaA if the initial quantity of radon occupied a volume of 0.65 cm^3 under normal conditions. Determine the number of radon and RaA atoms after five hours.

17. The radioisotope Cd^{118} undergoes the following transformations:



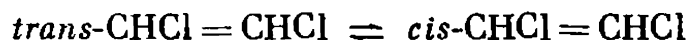
Assuming that the preparation contained initially 0.1 g of the first isotope only, determine (a) the weight of the stable isotope after an hour and (b) the decrease in the activity of the preparation after an hour.

18. The isotope Sb^{134} undergoes the following β -radioactive transformations:



Determine the relative numbers of the Te^{134} and I^{134} nuclei after an hour, assuming that the preparation contained initially only the first isotope.

19. Determine the rate constants of the forward and backward reactions

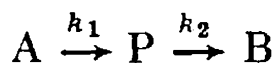


at 573 K, proceeding from the following concentrations of *trans*-CHCl=CHCl at different points in time:

$t, \text{ s}$	0	600	1080	∞
$c, \%$	95	82.88	75.24	41.89

Multivariate Problem

A consecutive first-order reaction proceeds as follows:



At 298 K, the specific rate of the reaction $\text{A} \rightarrow \text{P}$ is k_1 and that of the reaction $\text{P} \rightarrow \text{B}$ is k_2 , the initial concentration of substance A being $[\text{A}]_0$. Calculate (1) the coefficients of the maximum on the $[\text{P}] = f(t)$ curve (maximum concentration of intermediate product P and the time necessary to attain this concentration), (2) the time t_1 it takes for the concentration of the initial substance to reach $[\text{A}]_1$, (3) the concentrations $[\text{P}]$ and $[\text{B}]$ at instant t_1 , (4) the time it takes for the concentration of the intermediate product to become $[\text{P}]_1$, (5) the coordinates of the point of inflection of the $[\text{B}] = f(t)$ curve, and (6) the point of intersection of the $[\text{A}] = f(t)$ and $[\text{P}] = f(t)$ curves. Use the results to plot $[\text{P}] = f(t)$.

Variant	[A] ₀ , mole/litre	[A] ₁ , mole/litre	[P] ₁ , mole/litre	k ₁ , min ⁻¹	k ₂ , min ⁻¹
1	1	0.001	0.01	0.1	0.05
2	1	0.02	0.01	0.1	0.05
3	1	0.0015	0.01	0.1	0.05
4	1	0.002	0.01	0.1	0.05
5	1.5	0.001	0.01	0.1	0.05
6	2	0.001	0.02	0.1	0.05
7	2	0.001	0.015	0.1	0.05
8	2	0.001	0.012	0.1	0.05
9	1.5	0.015	0.02	0.1	0.05
10	1.5	0.015	0.01	0.1	0.05
11	1.5	0.015	0.015	0.1	0.05
12	1.5	0.015	0.012	0.1	0.05
13	1	0.001	0.01	0.12	0.07
14	1	0.001	0.02	0.12	0.07
15	1	0.001	0.015	0.12	0.07
16	1	0.001	0.01	0.1	0.07
17	2	0.002	0.02	0.12	0.05
18	2	0.002	0.02	0.12	0.05
19	2	0.002	0.01	0.12	0.05
20	2	0.002	0.01	0.1	0.07
21	1.2	0.015	0.01	0.1	0.08
22	1.2	0.015	0.01	0.1	0.08
23	1.2	0.015	0.01	0.1	0.08
24	1.2	0.015	0.01	0.1	0.08

CHAPTER 23

Temperature Dependence of the Reaction Rate

Basic Equations and Symbols

The temperature dependence of the reaction rate is approximated by the van't Hoff rule

$$\frac{k_{T_2}}{k_{T_1}} = \gamma^{\frac{T_2 - T_1}{10}} \quad (23.1)$$

where k_{T_1} and k_{T_2} are the rate constants at temperatures T_1 and T_2 , and γ is the temperature coefficient of the reaction rate constant (van't Hoff's coefficient); $\gamma = 2$ to 4 .

The temperature dependence of the reaction rate is also given by the Arrhenius equation whose differential form is

$$\frac{d \ln k}{dT} = \frac{E_{\text{exp}}}{RT^2} \quad (23.2)$$

and the integral form of this equation is

$$\log \frac{k_2}{k_1} = \frac{E_{\text{exp}}}{2.3R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \quad (23.3)$$

$$\log k = -\frac{E_{\text{exp}}}{2.3RT} + \text{const} \quad (23.4)$$

$$k = k_0 e^{-\frac{E_{\text{exp}}}{RT}} \quad (23.5)$$

where k_0 is a constant or a pre-exponential factor, and E_{exp} is the

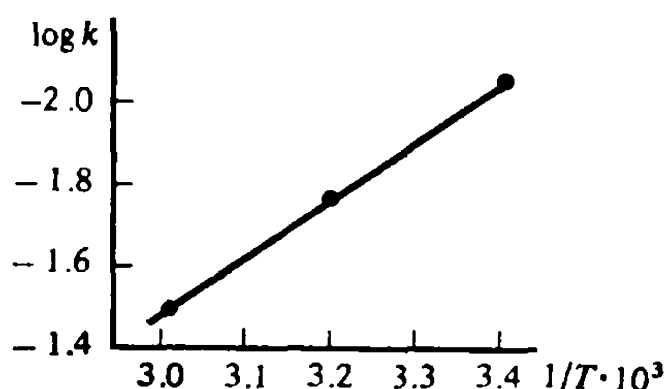


Fig. 43. $\log k$ versus $1/T$ for the copper oxidation reaction

activation energy (experimental activation energy). The activation energy and the temperature coefficient are related as

$$E = 2.3RT(T + 10) \log \gamma_T \quad (23.6)$$

where γ_T is van't Hoff's coefficient at temperature T .

$\log k = f(1/T)$ may give a straight line (Fig. 43), then

$$E = 2.3R \tan \alpha \quad (23.7)$$

where α is the slope angle of the straight line.

Exercises

1. In the presence of ions CN^- , benzaldehyde converts into benzoyl. Determine the activation energy for this conversion, proceeding from the following data:

T, K	313.2	323.1	333.2
k, min^{-1}	0.026	0.048	0.089

Solution. To find the activation energy use the equation

$$\log \frac{k_2}{k_1} = \frac{E}{2.303 \times 8.314} \frac{T_2 - T_1}{T_2 T_1}$$

hen,

$$E = \frac{2.303 \times 8.314 T_2 T_1}{T_2 - T_1} \log \frac{k_2}{k_1}$$

For 313.2 and 323.1 K,

$$E = \frac{2.303 \times 8.314 \times 313.2 \times 323.1}{9.9} \log \frac{0.048}{0.026} = 58\,785.2 \text{ J/mole}$$

For 333.2 and 323.1 K,

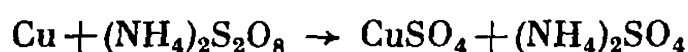
$$E = \frac{2.303 \times 8.314 \times 333.2 \times 323.1}{10.1} \log \frac{0.089}{0.048} = 54\,643.04 \text{ J/mole}$$

For 313.2 and 333.2 K,

$$E = \frac{2.303 \times 8.314 \times 313.2 \times 333.3}{20} \log \frac{0.089}{0.029} = 60\,040.4 \text{ J/mole}$$

$$E_{\text{mean}} = \frac{58\,785.2 + 54\,643.04 + 60\,040.4}{3} = 57\,822.88 \text{ J/mole}$$

2. Determine the activation energy of the reaction



The reaction rate constants at different temperatures are as follows:

$T, \text{ K}$	293.2	313.2	333.2
$k \times 10^3, \text{ litre mole}^{-1} \text{ min}^{-1}$	9.6	18.16	39.06

Solution. Determine the activation energy graphically with the aid of the equation

$$\log k = \log k_0 - \frac{E}{2.303 \times 8.314 T}$$

Present the experimental data as follows:

$\frac{1}{T} \times 10^3$	3.41	3.195	3.005
$\log k$	-2.018	-1.741	-1.475

and plot a graph (Fig. 43). Consequently,

$$\tan \alpha = \frac{-2.02 - 1.50}{3.41 - 3.02}$$

Determine the activation energy using Eq. (23.7):

$$E = -2.303 \times 8.314 \tan \alpha = -2.303 \times 8.314 \left(\frac{-2.02 - 1.50}{3.41 - 3.02} \right) = 25\,522.4 \text{ J/mole}$$

3. A solution of ethyl acetate at $c_1 = 0.01$ g-equiv/litre and 293 K is saponified with 0.002 *N* NaOH (c_2), the saponification being 10% complete within 23 min. The reaction is of the second order. How

will the above time period change if the reactant concentrations are reduced ten-fold and the temperature is raised by 15 °C?

Solution. Use the kinetic equation

$$k = \frac{1}{t} \frac{1}{(a-b)} \ln \frac{(a-x)b}{(b-x)a}$$

and substitution of $t = 23$ min, $a = c_1 = 0.01$ g-equiv/litre, $b = c_2 = 0.002$ g-equiv/litre, and $x = 10\%$ of c_1 , i.e. $x = 0.001$ g-equiv/litre, gives

$$k = \frac{1}{23} \frac{1}{0.01-0.002} 2.3 \log \frac{(0.01-0.001)0.002}{(0.002-0.001)0.01} = 3.19$$

When all concentrations are reduced ten-fold, $c_1 = 0.001$ g-equiv/litre, $c_2 = 0.0002$ g-equiv/litre, and $x = 0.0001$ g-equiv/litre. Substitution of these values into the kinetic equation for $k = 3.19$ gives

$$k = \frac{1}{t} \frac{1}{0.001-0.0002} 2.3 \log \frac{(0.001-0.0001)0.0002}{(0.0002-0.0001)0.001}$$

Hence, $t = 230$ min. Assuming that increasing the temperature by 10 °C doubles the reaction rate, $k_{T+10} = 2k_T$. Consequently, if the reaction temperature changes in the arithmetic progression $T = 10(n-1)$, the reaction rate will change in a geometric progression: $k = 2^{n-1}$ (n being the ordinal number of the progression term). Take the logarithm:

$$\log k = (n-1) \log 2$$

and substitute the value of $(n-1)$:

$$k = T/10 \log 2$$

Derive the relationship between k and T by differentiating $d \ln k / dT = 0.0301 \times 2.3$. Integration gives

$$\log k = 0.0301T + \text{const}$$

Hence,

$$\log \frac{k}{k_1} = 0.0301 (T - T_1), \quad (T - T_1) = 15^\circ, \quad k_1 = 3.19, \quad k_{T+15} = 9.04$$

and

$$kt = \frac{1}{a-b} \log \frac{(a-x)b}{(b-x)a}$$

$$k_1 t_1 = \frac{1}{a-b} \log \frac{(a-x)b}{(b-x)a}$$

The right-hand sides are equal by definition, therefore, $kt = k_1 t_1$ or $k/k_1 = t_1/t$. Consequently,

$$t = \frac{3.19}{9.6} 23 = 8.1 \text{ min} = 486 \text{ s}$$

Problems

1. The following first-order reaction rate constants have been derived for a thermal dissociation reaction:

$T, \text{ K}$	823	833	843	853	863	873	883	893	903
$k \times 10^{-5}, \text{ s}^{-1}$	2.5	4.7	8.2	12.3	23.1	35.3	57.6	92.4	141.5

Plot k versus T and $\log k$ versus $1/T$. Calculate the activation energy and pre-exponential factor.

2. The rate constants of a reaction in which an organic acid dissociates in an aqueous solution are as follows:

$T, \text{ K}$	273.2	293.2	313.2	333.2
$k \times 10^5, \text{ min}^{-1}$	2.46	47.5	576	5480

Plot $\log k$ versus $1/T$ and determine the activation energy. Calculate the constant k_0 in the equation $k = k_0 e^{-E_a/RT}$ and the half-time for the reaction at 373.2 K if the reaction is of the first order.

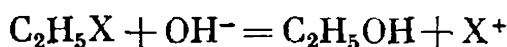
3. Two reactions of the same order have equal pre-exponential factors but their activation energies differ by 41.9 kJ/mole. Calculate the ratios between the rate constants of these reactions at 600 K.

4. The alkaline saponification of ethyl acetate is characterized by the following rate constants at different temperatures:

$T, \text{ K}$	273	293	298
$k, \text{ min}^{-1} \text{ mole}^{-1} \text{ litre}$	1.17	5.08	6.56

Calculate the activation energy and the half-time of the reaction at 298 K if the amounts of the reacting acetic ester solution and alkali are (a) 0.025 mole/litre and (b) 0.0125 mole/litre.

5. In an alcohol solution involved in the reaction



where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, the rate constants can be calculated using the following equations:

for the chloride:

$$k_1 = 0.793 \times 10^{10} T^{1/2} e^{-23\,000/RT}$$

for the bromide:

$$k_2 = 1.28 \times 10^{10} T^{1/2} e^{-21\,000/RT}$$

for the iodide:

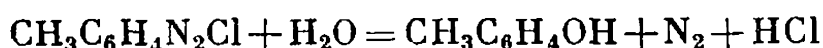
$$k_3 = 2.70 \times 10^{10} T^{1/2} e^{-21\,000/RT}$$

Calculate the rate constants and their ratio at 298 K, from which the dependence of the halide's mobility on its nature can be inferred.

6. The dissociation of a substance is a first-order reaction with an activation energy of 231 kJ/mole. At 300 K, this substance dissociates

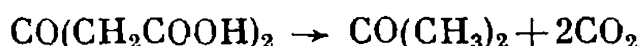
at a rate of 95% within an hour. Calculate the temperature at which the dissociation rate of the substance is 0.1% per minute.

7. A diazonium salt dissociates according to the equation



The dissociation process is a first-order reaction whose rate constants at 297.9 and 303.2 K are 9×10^{-3} and $13 \times 10^{-3} \text{ min}^{-1}$, respectively. Calculate the rate constant for 308.2 K and the time it takes for the dissociation of the diazonium salt to be 99% complete at the same temperature.

8. The rate constant of dissociation of acetone dicarboxylic acid



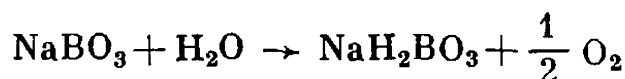
which is a first-order reaction, is $k_1 = 2.46 \times 10^5 \text{ min}^{-1}$ at $T_1 = 273.2 \text{ K}$ and $k_2 = 5.76 \times 10^{-3} \text{ min}^{-1}$ at $T_2 = 313.2 \text{ K}$. Calculate the time it takes for the reaction to be 70% complete at $T = 323.2 \text{ K}$.

9. The half-life of a substance in a first-order reaction is 100 min at 323.2 K and 15 min at 353.2 K. Calculate the temperature coefficient of the rate constant of this reaction.

10. The rate constant of saponification of ethyl acetate with NaOH is 2.37 at 282.6 K and 3.204 at 287.6 K. At what temperature will the rate constant equal four?

11. A solution contains 0.1 mole of ethyl acetate and 0.1 mole NaOH. The saponification of the acetic ester is 10% complete within 15 min at 283.2 K and 20% complete within the same period of time at 298.2 K. Calculate the amount of the ester that will be saponified within 5 min at 313.2 K.

12. The dissociation of sodium perborate



is a first-order reaction. The reaction rate constants at $T_1 = 303.2 \text{ K}$ and $T_2 = 308.2 \text{ K}$ are 2.2×10^{-3} and $4.1 \times 10^{-3} \text{ min}^{-1}$, respectively. Calculate the activation energy of the reaction and the time it will take for 99.99% of sodium perborate to dissociate at $T_3 = 313.2 \text{ K}$.

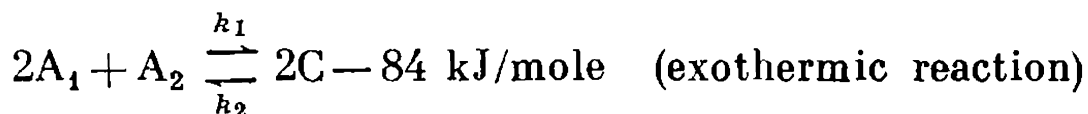
13. Isopropyl ether vapour isomerizes into allyl acetone in a first-order reaction. The temperature dependence of the rate constant (s^{-1}) is given by the equation $k = 5.4 \times 10^{11} \times e^{-29300/RT}$. How much time will it take for the partial pressure of allyl acetone to reach 300 mm Hg at 423 K if the initial pressure of isopropyl ether is 760 mm Hg?

14. The rate constants of a second-order reaction at 328.2 and 298.2 K are, respectively, 10^{-2} and $10^{-3} \text{ min}^{-1} \text{ mole}^{-1} \text{ litre}$. Calculate the rate of this reaction at 343.2 K at its onset if the initial con-

centrations of the two substances are the same and equal to 0.01 mole/litre.

15. A second-rate reaction ($A_1 + A_2 \rightarrow \text{products}$) is 90% complete at $[A_1]_0 = [A_2]_0 = 0.1$ mole/litre within 200 min at 300.2 K and within 40 min at 320.2 K. Calculate the time it will take for the reaction to be 99% complete at 330 K and $[A_1]_0 = [A_2]_0 = 0.01$ mole/litre.

16. A reversible reaction proceeds according to the stoichiometric equation



At 473 K, the rate of the forward reaction obeys the law $d[A_1]/dt = k_1 [A_1]^2$ and the temperature dependence of the reaction rate is given by the equation

$$\log k_1 = 10.42 - 19\,700/T$$

k_1 is given in litre mole⁻¹ s⁻¹). Derive the law to be obeyed by the rate of the backward reaction. Determine the activation energy of the backward reaction. Calculate the change in the entropy of the reaction and k_2 at 473 and 573 K if the equilibrium constant at 473 K is $K_p = 6.2 \times 10^3$ atm⁻¹. The rate of the zeroth-order reaction depends on the concentration of substance A_2 . Will this hold true for all concentrations of substances A_1 and A_2 ?

17. The rate at which substance A is spent in a reaction is given by the equation $-d[A]/dt = k[A]^3$. At $T_1 = 333$ K, $k = 4.20 \times 10^{-6}$ (the concentration of substance A is expressed in terms of pressure in mm Hg) and at $T_2 = 473$ K, $k = 1.4 \times 10^{-4}$ (the concentration being given in mm Hg). Calculate the activation energy and the Arrhenium (pre-exponential) factor as well as the constants k at 333 and 473 K if the concentration of substance A is given in mole/litre. Determine the activation energy and pre-exponential factor if the reaction rate is given in mole litre⁻¹ s⁻¹. Find out whether the determined energy will be the true activation energy of the reaction.

18. The isomerization reaction $A \rightleftharpoons B$ proceeds to completion at 338 K. The half-life of substance A was measured for two initial concentrations of the latter: $c_{0,1}$ and $c_{0,2} = 2c_{0,1}$, and it was found that the order of the reaction is 4/3 with respect to component A. The accuracy of determining the concentration of A is $\pm 2\%$, and the error in determining the half-life is negligibly small. The temperature was maintained to within $\pm 0.1^\circ$, and the activation energy was 840 kJ/mole. What is the accuracy of determining the half-life of substance A? Are the measurements accurate enough to distinguish the reaction order of 3/2 from that of 4/3?

19. For the dimerization of butadiene, $\log k = 7.673 - 5680/T$, where k is given in litre mole⁻¹ s⁻¹. What is the fraction of the butadiene molecules present in the system that has the energy sufficient for the reaction to take place at 573 and 723 K?

20. For the dissociation of phosphine according to the equation $4\text{PH}_3 \rightarrow \text{P}_4 + 6\text{H}_2$, the temperature dependence of the reaction rate is as follows:

$$\log k = -\frac{18\,953}{T} + 2 \log T + 12.130$$

Proceeding from these data, determine the temperature dependence of the activation energy and the activation energy proper at 800 K.

21. The kinetics of pyrolysis of ethyl bromide and *n*-propyl bromide was studied in the gas phase, using toluene as the gas carrier, at different temperatures. It was established that the pyrolysis is a first-order reaction. The following values were found for the rate constants:

T , K	800	833	877	900
k_1 , s ⁻¹	0.0361	0.141	0.662	1.410
T , K	794	806	855	881
k_2 , s ⁻¹	0.110	0.192	1.126	2.708

where k_1 is the rate constant of ethyl bromide pyrolysis and k_2 is the dissociation rate constant. Proceeding from these data, (a) determine graphically the energy of activation and the pre-exponential factor for the two reactions and (b) derive analytically the temperature dependence of the rate constant.

22. The rate constants of the reaction $2\text{HI} \xrightleftharpoons[k_2]{k_1} \text{I}_2 + \text{H}_2$ have the following values (cm³ mole⁻¹ s⁻¹): $k_1 = 0.259$ at 666.8 K, $k_1 = 1.242$ at 698.6 K, $k_2 = 15.59$ at 666.8 K, and $k_2 = 67.0$ at 698.6 K. Proceeding from these values, determine (a) the temperature dependence of the rate constants of the forward and backward reactions, (b) the temperature dependence of the equilibrium constant of HI dissociation, (c) the equilibrium constant at 553 and 763 K, and compare the results with the experimental data: $K_c = 1.173 \times 10^{-2}$ at 553 K and $K_c = 2.182 \times 10^{-2}$ at 763 K.

Multivariant Problem

Given the rate constants of a reaction at two temperatures, determine the activation energy, the rate constant at temperature T_3 , the temperature coefficient of the reaction rate, and the amount of the reactant spent within the time period t if the initial concentrations are c_0 . Remember that the reaction order coincides with molarity.

Variant	Reaction	T_1, K	$k_1, \text{min}^{-1} \text{ litre}^{-1}$	T_2, K	$k_2, \text{min}^{-1} \text{ litre}^{-1}$	T_3, K	t, min	$c_0, \text{mole/litre}$
1	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	574.5	0.0856	497.2	0.00036	483.2	60	0.09
2	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	550.7	0.0159	524.6	0.0026	568.2	10	0.10
3	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	599.0	0.00146	672.0	0.0568	648.2	28	2.83
4	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	683.0	0.0659	716.0	0.375	693.2	27	1.83
5	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	456.2	0.942×10^{-6}	700.0	0.0031	923.2	17	2.38
6	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	628.4	0.809×10^{-4}	780.4	0.1059	976.2	18	1.87
7	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1525.2	47059	1251.4	1073	1423.2	45	2.83
8	$2\text{NO}_2 \rightarrow \text{N}_2 + 2\text{O}_2$	986.0	6.72	1165.0	977.0	1053.2	65	1.75
9	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$	298.2	0.00203	288.2	0.475×10^{-3}	338.2	32	0.93
10	$\text{PH}_3 \rightarrow \text{P}_{(g)} + \frac{3}{2} \text{H}_2$	953.2	0.0183	918.2	0.0038	988.2	80	0.87
11	$\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$	552.2	0.609×10^{-4}	593.2	0.132×10^{-2}	688.2	35	2.50
12	$\text{KClO}_3 + 6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{KCl} + 3\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}^*$	283.2	1.00	305.2	7.15	383.2	35	1.67
13	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	288.2	0.00031	313.2	0.00815	303.2	89	3.85

(Table concluded)

Variant	Reaction	T_1, K	$k_1, \text{min}^{-1} \text{ litre}^{-1} \text{ mole}^{-1}$	T_2, K	$k_2, \text{min}^{-1} \text{ litre}^{-1} \text{ mole}^{-1}$	T_3, K	t, min	$c_0, \text{mole/litre}$
14	$\text{COCl}_2 \rightarrow \text{CO} + \text{Cl}_2$	655.0	0.53×10^{-2}	745.0	67.6×10^{-2}	698.2	104.5	0.80
15	$\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_5\text{OCH}_2\text{I} + \text{NaI}$	273.3	0.0336	303.2	2.125	288.2	10	0.87
16	$\text{CH}_2\text{OHCH}_2\text{Cl} + \text{KOH} \rightarrow \text{CH}_2\text{OHCH}_2\text{OH} + \text{KCl}$	297.7	0.68	316.8	5.23	303.2	18	0.96
17	$\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OHCOOH} + \text{HCl}$	353.2	0.222×10^{-4}	403.2	0.00237	423.2	26	0.50
18	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{CO}_2\text{Na} + \text{C}_2\text{H}_5\text{OH}$	282.6	2.307	318.1	21.65	343.2	15	0.95
19	$\text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH}$ (in aqueous solution the catalyst is 0.1 N HCl)	298.2	0.653×10^{-3}	308.2	1.663×10^{-3}	313.2	25	1.60
20	$\text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH}$	298.2	16.09×10^{-3}	308.2	37.84×10^{-3}	323.2	80	2.96
21	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$	273.2	2.056×10^{-5}	313.2	109.4×10^{-5}	298.2	67	3.55
22	$2\text{CH}_2\text{O} + \text{NaOH} \rightarrow \text{HCO}_2\text{Na} + \text{CH}_3\text{OH}$	323.2	5.5×10^{-3}	358.2	294.0×10^{-3}	338.2	5	0.50
23	$(\text{CH}_3)_2\text{SO}_4 + \text{NaI} \rightarrow \text{CH}_3\text{I} + \text{Na}(\text{CH}_3)\text{SO}_4$	273.2	0.029	298.2	1.04	285.8	100	3.89
24	$\text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OC}_2\text{H}_5 + \text{HBr}$	298.2	1.44	338.2	2.01	318.2	90	2.67
25	$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$	298.2	0.765	328.2	35.5	313.2	15	1.85

* The reaction is of the first order.

CHAPTER 24

Basic Theory Behind Calculation of Reaction Rate Constant

Basic Equations and Symbols

The reaction rate w for similar gaseous molecules is calculated using the equation

$$w = Z'_{AA} e^{-E/RT} \quad (24.1)$$

in which E is the activation energy, and Z'_{AA} is the number of collisions between molecules of gas A within a volume of 1 cm^3 per second;

$$Z'_{AA} = \frac{1}{2} \sqrt{2} \pi \sigma^2 N^2 \bar{u} \quad (24.2)$$

$Z'_{AA} e^{-E/RT}$ is the number of active collisions within 1 cm^3 per second, N is the number of molecules within 1 cm^3 , and \bar{u} is the mean arithmetic velocity of the molecules.

In the case of a reaction $A + B \rightarrow \text{products}$, the rate w of interaction between dissimilar molecules A and B will be

$$w = Z''_{AB} e^{-E/RT} \quad (24.3)$$

where $Z''_{AB} e^{-E/RT}$ is the number of active collisions between molecules A and B within 1 cm^3 per second;

$$Z''_{AB} = \pi \left(\frac{\sigma_A + \sigma_B}{2} \right)^2 \sqrt{\frac{8RT}{\pi} \left(\frac{M_A + M_B}{M_A M_B} \right)} N_A N_B \quad (24.4)$$

where σ_A and σ_B are the gas-kinetic diameters of molecules A and B, M_A and M_B are the molecular weights of substances A and B, and Z''_{AB} is the number of collisions between molecules A and B within 1 cm^3 per second. The quantity $\pi \left(\frac{\sigma_A + \sigma_B}{2} \right)^2$ (collision cross section in Eq. (24.4)) for gases is determined from the viscosity of the substance. For an individual gas, the collision cross section will be $\pi \sigma^2$:

$$\pi \sigma^2 = \frac{M \bar{u}}{3 \pi \eta N_A} \quad (24.5)$$

Hence, the molecular diameter will be

$$\sigma = \sqrt{\frac{M \bar{u}}{3 \pi \eta N_A}} \quad (24.6)$$

For a binary mixture of gases, the collision cross section will be

$$\pi (\sigma_A + \sigma_B)^2 = \pi \left[\sqrt{\frac{M_A \bar{u}_A}{3 \pi \eta_A N_A}} + \sqrt{\frac{M_B \bar{u}_B}{3 \pi \eta_B N_B}} \right]^2 \quad (24.7)$$

In chemical kinetics studies, the collision cross section can be evaluated accurately enough if it is assumed that molecules are densely packed in a liquid or solid. The volume occupied by one mole (molar volume) is M/d , d being the substance density, g/cm^3 . In the case of dense packing, a sphere with radius r occupies a volume equal to $8r^3/\sqrt{2}$. Consequently,

$$r = \frac{1}{2} \sqrt[3]{1.41 \times 1.66 \times 10^{-24} \frac{M}{d}} = 0.665 \times 10^{-8} \left(\frac{M}{d} \right)^{1/3}$$

and

$$\pi (\sigma_A + \sigma_B)^2 = 1.39 \times 10^{-16} \left[\left(\frac{M_A}{d_A} \right)^{1/2} + \left(\frac{M_B}{d_B} \right)^{1/3} \right]^2 \quad (24.8)$$

In the case of interaction between similar and dissimilar molecules, the rate constant is given by the equations

$$k = \frac{w_2}{N^2} \left(\text{or } \frac{w}{N_A N_B} \right) = Z_0 e^{-E/RT} \quad (24.9)$$

where k is given in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and

$$k = Z_0 \times 10^3 N_A e^{-E/RT} \quad (24.10)$$

where Z_0 is the collision factor, and k in Eq. (24.10) is given in $\text{litre mole}^{-1} \text{ s}^{-1}$. When similar molecules collide, the collision factor is calculated using the equation

$$Z_0 = \frac{1}{2} \sqrt{2} \pi \sigma^2 \sqrt{\frac{8kT}{\pi m}} \quad (24.11)$$

where Z_0 is expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In the case of dissimilar molecules, the collision factor is given by the equation

$$Z_0 = \pi \left(\frac{\sigma_A + \sigma_B}{2} \right)^2 \sqrt{\frac{8RT}{\pi} \frac{M_A + M_B}{M_A M_B}} \quad (24.12)$$

in which Z_0 is expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The refined form of the equation for calculating the rate constant is

$$k = p Z_0 e^{-E/RT} \quad (24.13)$$

where p is the steric factor.

The pre-exponential factor in Eq. (23.5) is

$$k_0 = p Z_0 \quad (24.14)$$

according to the binary collision theory.

According to the activated complex (transition state) theory, the reaction rate constant is determined with the aid of the Eyring equation (for bimolecular reactions)

$$k = \kappa \frac{kT}{h} \frac{Q_{\text{act}}}{Q_A Q_B} e^{-E_0/RT} \quad (24.15)$$

in which E_0 is the activation energy at absolute zero, and Q_{act} , Q_A , and Q_B are the molecular statistical sums (molecular sums over states) for the activated complex and initial substances A and B.

The quasi-thermodynamic form of the Eyring equation is

$$k = \kappa e^x \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-E/RT} \quad (24.16)$$

where κ is the barrier factor, $x = 1$ for monomolecular reactions and $x = 2$ for bimolecular reactions, ΔS^\ddagger is the entropy of activation, and E is the experimental activation energy:

$$E = RT + \Delta H^\ddagger \quad (24.17)$$

where ΔH^\ddagger is the enthalpy of activation. The constants have the following dimensions: time^{-1} for monomolecular reactions, and $\text{volume weight}^{-1} \text{time}^{-1}$ for bimolecular reactions. According to the transition state theory, the pre-exponential factor in Eq. (23.5) is given by the equation

$$k_0 = \kappa e^x \frac{kT}{h} e^{\Delta S^\ddagger/R} \quad (24.18)$$

in which the dimensions of k are $\text{volume weight}^{-1} \text{time}^{-1}$.

Exercises

1. The dissociation of hydrogen iodide is a bimolecular reaction whose activation energy is $E = 1848 \times 10^2 \text{ J/mole}$. It proceeds at 566.2 K, the diameter of an HI molecule, calculated with reference to viscosity, is $3.5 \times 10^{-10} \text{ m}$, and the concentration of hydrogen iodide is 1 mole/litre. Determine the rate constant of the reaction at 566.2 K.

Solution. Calculate the rate constant at 566.2 K on the basis of the number of collisions. Determine the mean velocity \bar{u}_a using the equation

$$\begin{aligned} \bar{u}_a &= \sqrt{\frac{8RT}{\pi M^*}} = \sqrt{\frac{8 \times 8.314 \times 10^7 \times 566.2}{3.14 \times 128/2}} = 4.33 \times 10^4 \text{ cm/s} \\ &= 4.33 \times 10^2 \text{ m/s} \end{aligned}$$

Calculate the number of HI molecules per 1 cm^3 . Since the concentration of hydrogen iodide is 1 mole/litre, the number N of its molecules per cubic centimetre will be

$$N = \frac{6.02 \times 10^{23}}{10^3} = 6.02 \times 10^{20} \text{ molecules}$$

The number of collisions will then be

$$Z = \frac{\sqrt{2}}{2} \pi (2r_A)^2 \bar{u}_a n^2$$

$$Z = \frac{1.41}{2} 3.14 (3.5 \times 10^{-8})^2 \times 4.33 \times 10^4 \times (6.02 \times 10^{23})^2 = 4.25 \times 10^{31}$$

Determine the number of molecules in the active state:

$$\frac{Z_{\text{act}}}{Z_{\text{tot}}} = e^{-E/RT} = e^{-\frac{1848 \times 10^2}{8.314 \times 566}} = 8.42 \times 10^{-18}$$

The number of colliding molecules pZ_0 is twice the number of collisions Z , therefore,

$$pZ_0 = 4.25 \times 10^{31} \times 2 = 8.5 \times 10^{31} \text{ molecules/cm}^3$$

In order to express the number of molecular collisions in terms of

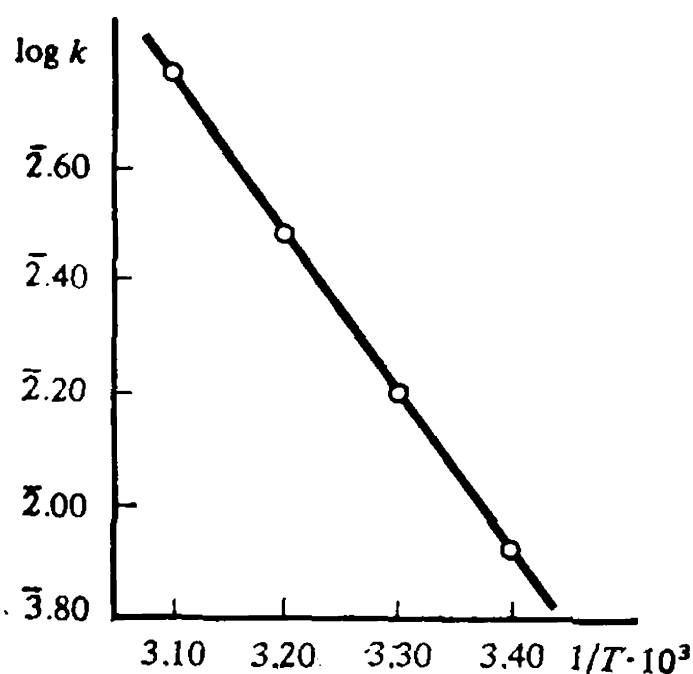


Fig. 44. $\log k$ versus $1/T$ for the reaction $\text{C}_5\text{H}_5\text{N} + \text{CH}_3\text{I} = [\text{C}_5\text{H}_5\text{NCH}_3]^+\text{I}^-$

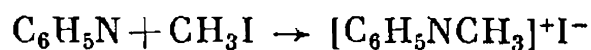
the number of moles within 1 cm^3 per second, divide the above result by the Avogadro number:

$$pZ_0 = 8.5 \times 10^{31} / 6.02 \times 10^{23} = 1.41 \times 10^7$$

Substitution of the calculated value into the equation $k = pZ_0 e^{-E/RT}$ gives

$$k = 1.41 \times 10^7 \times 8.42 \times 10^{-18} = 11.9 \times 10^{-11} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

2. The kinetics of the reaction between methyl iodide and pyridine in tetrachloroethane



was studied with the following results:

$T, \text{ K}$	293.1	303.1	313.1	323.2
$k \times 10^2, \text{ litre mole}^{-1} \text{ min}^{-1}$	0.713	1.5	3.5	5.89

The reaction is irreversible and of the second order. Calculate the activation energy and the steric factor if the density of pyridine is $d_p = 0.98 \text{ g/cm}^3$ and that of methyl iodide, $d_{\text{m.i.}} = 2.28 \text{ g/cm}^3$.

Solution. Plot k versus T in Arrhenius' coordinates (Fig. 44). Determine the activation energy from the slope of the resultant straight line:

$$E = 2.3R \tan \alpha = 2.3 \times 8.314 \times 1.43 \times 2000 = 54\,689 \text{ J}$$

where $\tan \alpha$ represents the ratio between the increments on the X and Y axes with due account for the appropriate scale. Write the equation for the straight line:

$$\log k = \log (pZ_0) - |\tan \alpha| \xi 1/T \times 10^3 = \log (pZ_0) - 2.861/T \times 10^3$$

Then take the coordinates of any point on the straight line, for example, $\log k = \bar{3}.88$ at $1/T \times 10^3 = 3.40$, and calculate

$$\log (pZ_0) = \bar{3}.88 + 2.86 \times 3.40 = \bar{3}.88 + 9.73 = 7.61$$

$$pZ_0 = 4.1 \times 10^7 \text{ litre mole}^{-1} \text{ min}^{-1} = \frac{4.1 \times 10^7}{60 \times 6.02 \times 10^{23}} \text{ cm}^3/\text{s} \\ = 1.13 \times 10^{-15} \text{ cm}^3/\text{s}$$

Use the equation

$$Z_0 = \pi (r_A + r_B)^2 \left(\frac{8kT}{\pi m^*} \right)^{1/2}$$

to calculate Z_0 . Having determined the values of pZ_0 from the experimental data, calculate the steric factor of the reaction. More specifically, the molecular weight of pyridine is $M_p = 79$, its density is $d_p = 0.98 \text{ g/cm}^3$, while the molecular weight of methyl iodide is $M_{m.i.} = 142$ and its density is $d_{m.i.} = 2.28 \text{ g/cm}^3$. The reduced weight M^* will be

$$M^* = \frac{M_{m.i.} M_p}{M_{m.i.} + M_p} = \frac{79 \times 142}{221} = 50.7$$

The cross section of collision in a liquid or solid can be estimated with sufficient accuracy if the molecules are densely packed. The volume occupied by one mole (molar volume) is M/d . The volume of one sphere of radius r is $8r^3/\sqrt{2}$ in the case of dense packing, therefore,

$$r = \frac{1}{2} \sqrt[3]{1.41 \times 1.66 \times 10^{-24} M/d} = 0.665 \times 10^{-8} (M/d)^{1/3}$$

and the collision cross section is

$$\pi \left(\frac{\sigma_{m.i.} + \sigma_p}{2} \right)^2 = 1.39 \times 10^{-16} \left[\left(\frac{M_{m.i.}}{d_{m.i.}} \right)^{1/3} + \left(\frac{M_p}{d_p} \right)^{1/3} \right]^2$$

Hence,

$$\pi \left(\frac{\sigma_{m.i.} + \sigma_p}{2} \right)^2 = 1.39 \times 10^{-16} \left[\left(\frac{79}{0.98} \right)^{1/3} + \left(\frac{142}{2.28} \right)^{1/3} \right]^2 \\ = 9.5 \times 10^{-15} \text{ cm}^2$$

The mean relative velocity of molecules at 308 K will be

$$\bar{u} = \sqrt{\frac{8 \times 8.31 \times 10^7 \times 308}{3.14 \times 50.7}} = 3.58 \times 10^4 \text{ cm/s}$$

Then,

$$Z_0 = \pi \left(\frac{\sigma_{m.l.} + \sigma_p}{2} \right)^2 \bar{u} = 3.58 \times 10^4 \times 9.5 \times 10^{-15} = 3.4 \times 10^{-10} \text{ cm}^3/\text{s}$$

Consequently, the steric factor is

$$p = 1.13 \times 10^{-15} / 3.4 \times 10^{-10} = 3.3 \times 10^{-6}$$

3. Proceeding from the theories of collision and transition state, demonstrate that $k_0 = Z_0$. Use the data from the handbook to cal-

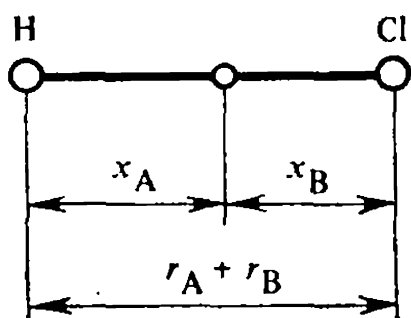


Fig. 45. Determination of the coordinates of the centre of gravity for the HCl molecule

culate, with the above theories in view, the pre-exponential factor for the reaction $\text{H} + \text{Cl} \rightarrow \text{HCl}$ at 298 K.

Solution. When two atoms react, the initial particles lack the rotational component of the statistical sum, and the activated complex is essentially a diatomic particle. The moment of inertia I of the activated complex, with respect to the centre of gravity, is

$$I = m_{\text{H}}x_{\text{H}}^2 + m_{\text{Cl}}x_{\text{Cl}}^2$$

where x_{H} and x_{Cl} are the distances between the centres of the H and Cl atoms, respectively, and that of the molecule (Fig. 45). According to the definition of the centre of gravity, $m_{\text{H}}x_{\text{H}} = m_{\text{Cl}}x_{\text{Cl}}$. In view of the fact that $x_{\text{H}} + x_{\text{Cl}} = r_{\text{H}^+} + r_{\text{Cl}}$, transformation gives

$$x_{\text{H}} = \frac{m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} (r_{\text{H}} + r_{\text{Cl}})$$

$$x_{\text{Cl}} = \frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{Cl}}} (r_{\text{H}} + r_{\text{Cl}})$$

$$I = \frac{m_{\text{H}}m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} (r_{\text{H}} + r_{\text{Cl}})^2 = m^* (r_{\text{H}} + r_{\text{Cl}})^2$$

For a diatomic particle having two rotational degrees of freedom,

$$(Z^{\neq})_{\text{rot}} = \frac{8\pi^2 kT}{h^2} I = \frac{8\pi^2 kT}{h^2} m^* (r_{\text{H}} + r_{\text{Cl}})^2 = \frac{8\pi kT}{h^2} m^* \pi (r_{\text{H}} + r_{\text{Cl}})^2$$

Hence, according to the transition state theory and provided that the vibrational statistical sum equals unity for this reaction,

$$k_0 = \frac{h^2}{(2\pi)^{3/2} k^{1/2} (m^*)^{3/2} T^{1/2}} \frac{Z_{\text{rot}}^\ddagger}{(Z_{\text{H}})_{\text{rot}} (Z_{\text{Cl}})_{\text{rot}}} = \frac{h^2}{(2\pi)^{3/2} k^{1/2} (m^*)^{3/2} T^{1/2}} Z_{\text{rot}}^\ddagger$$

$$= \frac{h^2}{(2\pi)^{3/2} k^{1/2} (m^*)^{3/2} T^{1/2}} \frac{8\pi kT}{h^2} m^* \pi (r_{\text{H}} + r_{\text{Cl}})^2 = \pi (r_{\text{H}} + r_{\text{Cl}})^2 \left(\frac{8kT}{\pi m^*} \right)^{1/2}$$

If $p = 1$, then

$$k_0 = \pi (r_{\text{H}} + r_{\text{Cl}})^2 \left(\frac{8kT}{\pi m^*} \right)^{1/2}$$

Thus, for a reaction involving two atoms, the pre-exponential factor calculated by the activated complex method coincides with the collision factor. According to the handbook, $r_{\text{H}} = 2.08 \times 10^{-8}$ cm and $r_{\text{Cl}} = 1.81 \times 10^{-8}$ cm. Consequently,

$$Z_0 = 3.14 (1.81 + 2.08)^2 10^{-16} \sqrt{\frac{8 \times 8.31 \times 10^7 \times 298}{3.14}} = 1.36 \times 10^{-9} \text{ cm}^3/\text{s}$$

4. Calculate the pre-exponential and steric factors for the reaction $\text{C}_2\text{H}_4 + \text{Cl} \rightarrow \text{C}_2\text{H}_4\text{Cl}$ at 298 K, using models of the activated complex and initial particles, shown in Figs. 46 and 47.

Solution. To calculate the pre-exponential and steric factors it is necessary to find the molecular statistical sums of the translatory, rotational, and vibrational motions for the reactants and activated complex. Determination of the rotational statistical sums is based on the moments of inertia, and that requires knowledge of the configuration of the initial particles and activated complex. The rotational statistical sums for the activated complex can be calculated only if certain assumptions are made as regards its structure. This can be done with a reasonable degree of accuracy because the activated complex is an intermediate state between the initial particles and the particles of the reaction products.

In constructing the model of the activated complex, the following assumptions are made: (1) the length of the C—C bond falls between those of the C—C bonds in ethylene and in the resulting free radical $\text{C}_2\text{H}_4\text{Cl}$; (2) the $\text{H}_1\text{C}_1\text{C}_2$, $\text{H}_2\text{C}_1\text{C}_2$, and $\text{H}_1\text{C}_1\text{H}_2$ angles (Fig. 47) are equal and constitute 115° (i.e. between 120° in ethylene and 109° in $\text{C}_2\text{H}_4\text{Cl}$); (3) the Cl atom approaches the ethylene molecule following a direction perpendicular to the plane of the latter, and the ClC_1C_2 angle in the activated complex (Fig. 47) equals 100° (i.e. between the right angle and 109° in the resulting free radical). The distance between Cl and C_1 is assumed to equal 2.00 Å (which is somewhat longer than in $\text{C}_2\text{H}_4\text{Cl}$). The hypothetical configuration of the activated complex is illustrated in Fig. 47.

To calculate the moments of inertia of ethylene and the activated complex it is convenient to select a system of coordinates with an

OX axis extending along the C—C bond, an OY axis lying in the plane of the ethylene molecule and perpendicular to the C—C bond, and an OZ axis perpendicular to the plane of the ethylene molecule and to the origin of coordinates, coinciding with the centre of the C—C bond. As regards ethylene, the origin of coordinates is at the

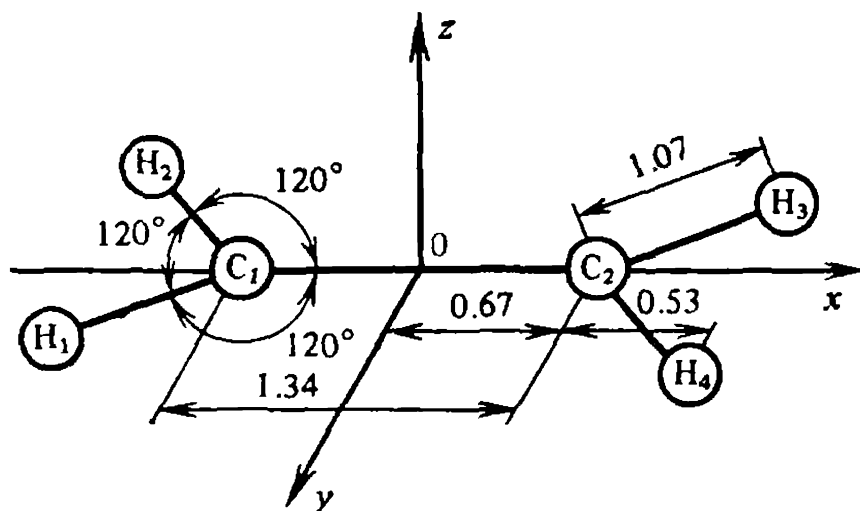


Fig. 46. Determination of the coordinates of the centre of gravity for the $\text{CH}_2=\text{CH}_2$ molecule

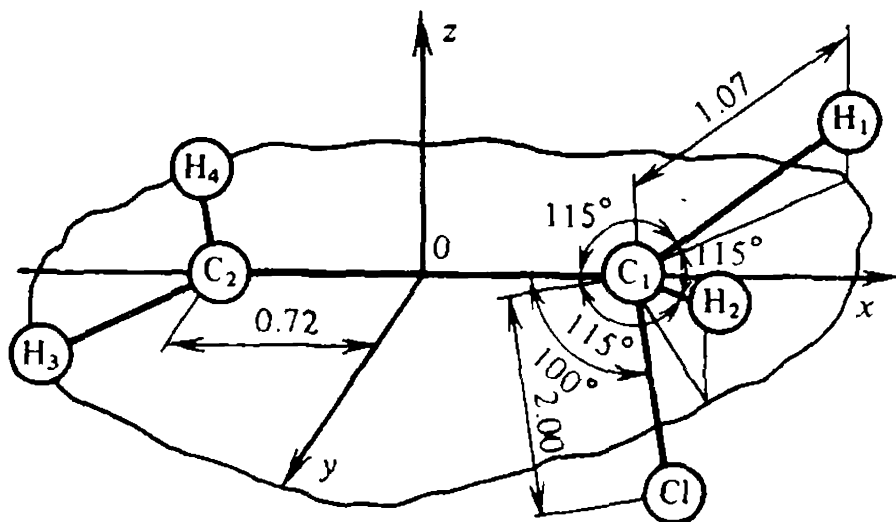


Fig. 47. Hypothetical structure of the activated complex

centre of gravity of the molecule and the coordinate axes follow the molecular axes of symmetry. Since ethylene has three mutually perpendicular axes of symmetry, they are also the principal axes of inertia and, consequently, solution of the problem boils down to calculation of the moments of inertia with respect to the three coordinate axes:

$$I_x^{(A)} = \sum M_i r_{xi}^2 = \sum M_i (z_i^2 + y_i^2)$$

$$I_y^{(A)} = \sum M_i r_{yi}^2 = \sum M_i (x_i^2 + z_i^2)$$

$$I_z^{(A)} = \sum M_i r_{zi}^2 = \sum M_i (x_i^2 + y_i^2)$$

The coordinates of the atoms are as follows:

	C ₁	C ₂	H ₁	H ₂	H ₃	H ₄
x_i	0.67	-0.67	-1.20	-1.20	1.20	1.20
y_i	0	0	0.93	-0.93	-0.93	0.93
z_i	0	0	0	0	0	0

$M_H = 1$, $M_C = 12$. Hence,

$$I_x^{(A)} = 4 \times 1 \times 0.93^2 = 3.46$$

$$I_y^{(A)} = 4 \times 1 \times 1.20^2 + 2 \times 12 \times 0.67^2 = 16.56$$

$$I_z^{(A)} = 4 \times 1 (1.20^2 + 0.93^2) + 2 \times 12 \times 0.67^2 = 20.0$$

$$I_A^A I_B^A I_C^A = I_x^A I_y^A I_z^A$$

To calculate the product of moments of inertia with respect to the principal axes of inertia for the activated complex use the formula

$$I_A I_B I_C = \begin{vmatrix} I_x & -I_{xy} & -I_{xz} \\ -I_{xy} & I_y & -I_{yz} \\ -I_{xz} & -I_{yz} & I_z \end{vmatrix}$$

where I_x , I_y , and I_z are the moments of inertia with respect to any three mutually perpendicular axes passing through the molecule's centre of gravity; I_{xy} , I_{xz} , and I_{yz} are the products of inertia;

$$I_{xy} = \sum M_i x_i y_i; \quad I_{xz} = \sum M_i x_i z_i, \quad I_{yz} = \sum M_i y_i z_i$$

Calculate the coordinates of atoms Cl, H₃, H₄, C₁, and C₂ using the stated bond lengths and angles. The coordinates of H₁ (x , y , z) and H₂ (x , $-y$, z) should be calculated in the following way. The length l of the line segment connecting the points with coordinates x_0 , y_0 , z_0 and x_1 , y_1 , z_1 is

$$l_1 = \sqrt{(x_1 - x_0)^2 + (y_1 - y_0)^2 + (z_1 - z_0)^2}$$

and the angle φ between two line segments with a common origin at the point (x_0, y_0, z_0) and ends at the points (x_1, y_1, z_1) and (x_2, y_2, z_2) can be determined from the formula

$$(x_1 - x_0)(x_2 - x_0) + (y_1 - y_0)(y_2 - y_0) + (z_1 - z_0)(z_2 - z_0) = l_1 l_2 \cos \varphi$$

Application of this expression to the line segments C₁H₁, C₁H₂, and C₁O gives the following equations for the coordinates x , y , and z of interest of atoms H₁ and H₂:

$$(x - 0.72)^2 + y^2 + z^2 = 1.07^2$$

$$(x - 0.72)^2 - y^2 + z^2 = 1.07 \times 0.72 \cos 115^\circ$$

$$-(x - 0.72) 0.72 = 1.07 \times 0.72 \cos 115^\circ$$

Solution of these equations gives the coordinates of H_1 and H_2 . Thus, the coordinates of the atoms are as follows:

	H_1	H_2	H_3	H_4	C_1	C_2	Cl
x_i	1.17	1.17	-1.25	-1.25	0.72	-0.72	1.07
y_i	-0.86	0.86	0.93	-0.93	0	0	0
z_i	0.45	0.45	0	0	0	0	-1.97

To find the coordinates of the centre of gravity use the equations

$$Z^* = \frac{\sum M_i x_i}{\sum M_i} = 0.6, \quad Y^* = \frac{\sum M_i y_i}{\sum M_i} = 0$$

$$Z^* = \frac{\sum M_i z_i}{\sum M_i} = -1.09$$

Consequently, in the system of coordinates associated with the centre of gravity,

	H_1	H_2	H_3	H_4	C_1	Cl
x_i	0.57	0.57	-1.85	-1.85	-1.32	0.47
y_i	-0.86	0.86	0.93	-0.93	0	0
z_i	-1.54	1.54	1.09	1.09	10.9	-0.88

Hence, $I_x^* = 66.3$, $I_y^* = 99.4$, $I_z^* = 39.5$; $I_{xy}^* = I_{yz}^* = 0$; $I_{xz}^* = -32.7$;

$$I_A^* I_B^* I_C^* = \begin{vmatrix} 66.3 & 0 & 32.7 \\ 0 & 99.4 & 0 \\ 32.7 & 0 & 39.5 \end{vmatrix} = 1.54 \times 10^5$$

Substitution of the values of rotational statistical sums into the equations gives

$$k_0 = \frac{h^2}{(2\pi)^{3/2} k^{1/2} (m^*)^{3/2} T^{1/2}} \frac{Z_{\text{rot}}^*}{(Z_A)_{\text{rot}} (Z_B)_{\text{rot}}}$$

and after reduction we have

$$k_0 = \frac{h^2}{(2\pi)^{3/2} k^{1/2} (m^*)^{3/2} T^{1/2}} \frac{(I_A^* I_B^* I_C^*)^{1/2}}{I_A^{(A)} I_B^{(A)} I_C^{(A)}}$$

then $k_0 = 4.8 \times 10^{-12} \text{ cm}^3/\text{s}$.

To determine the steric factor one must know the collision factor. The collision cross-section can be calculated on the basis of the viscosity data for Cl_2 and C_2H_4 : $\eta_{\text{Cl}_2} = 1.33 \times 10^{-3} \text{ Pa s}$ and $\eta_{\text{C}_2\text{H}_4} = 1.01 \times 10^{-3} \text{ Pa s}$. Use Eq. (24.6) to calculate the radius:

$$r = \frac{1}{2} \sqrt{\frac{M\bar{u}}{3\pi\eta N_0}}, \quad r_{\text{Cl}_2} = 2.63 \times 10^{-8} \text{ cm}, \quad r_{\text{C}_2\text{H}_4} = 2.4 \times 10^{-8} \text{ cm}$$

If it is assumed that the volume occupied by one Cl atom equals that occupied by the Cl_2 molecule, the linear dimensions of the Cl atom must be $\sqrt[3]{2}$ times smaller, as compared with the Cl_2 molecule;

$$r_{\text{Cl}} = 2.63 \times 10^{-8} \sqrt[3]{2} = 2.08 \times 10^{-8} \text{ cm}$$

Therefore,

$$Z_0 = 3.14 (2.43 + 2.08)^2 \times 10^{-16} \sqrt{\frac{8 \times 8.31 \times 10^7 \times 298}{3.14 \times 15.6}} = 4.45 \times 10^{-10} \text{ cm}^3/\text{s}$$

Hence, the steric factor is $p = k_0/Z_0 = 1.08 \times 10^{-2}$.

5. For the dissociation reaction $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$, the rate constants are $k_1 = 0.0108 \text{ mole litre}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$ at 1620 K and $k_2 = 0.030 \text{ mole litre}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$ at 1572 K. Calculate ΔH^\ddagger and ΔS^\ddagger at the mean temperature of 1572 K.

Solution. To calculate the entropy and heat of activation use the equation from the theory of absolute reaction rates, given in the logarithmic form:

$$\log k = \log \frac{k}{hR} + \frac{1}{2.3R} \left(\Delta S^\ddagger - \frac{\Delta H^\ddagger}{R} \right)$$

$$\log k = \log \frac{1.3805 \times 10^{-23}}{6.6238 \times 10^{-34} \times 0.08206} + \frac{1}{2.3 \times 8.314} \left(\Delta S^\ddagger - \frac{\Delta H^\ddagger}{R} \right)$$

$$\log \frac{1.3805 \times 10^{-23}}{6.6238 \times 10^{-34} \times 0.08206} = \log (2.5398 \times 10^{11}) = 11.4048$$

Write the equation for $\log k$ at $T = 1620$ K:

$$\log 0.0108 = -1.96658 = 11.4048 + \frac{\Delta S^\ddagger}{19.147} - \frac{\Delta H^\ddagger}{19.147 \times 1620} \quad (1)$$

and at $T = 1525$ K:

$$\log 0.0030 = -2.52288 = 11.4048 + \frac{\Delta S^\ddagger}{19.147} - \frac{\Delta H^\ddagger}{19.147 \times 1525} \quad (2)$$

To determine ΔS^\ddagger and ΔH^\ddagger solve equations (1) and (2) simultaneously,

$$\frac{\Delta H^\ddagger}{31\,018.4} - \frac{\Delta S^\ddagger}{19.147} = 13.37138$$

$$\frac{\Delta H^\ddagger}{29\,199.17} - \frac{\Delta S^\ddagger}{19.147} = 13.92768$$

Consequently, $\Delta H^\ddagger = 276\,993.62 \text{ J/mole}$ and $\Delta S^\ddagger = -85.038 \text{ J mole}^{-1} \text{ K}^{-1}$. It is to be assumed that the values of ΔS^\ddagger and ΔH^\ddagger for the mean reaction temperature (1572 K) remain the same as for 1620 and 1525 K.

Problems

1. A vessel is filled with nitrogen at 1.01×10^5 Pa and 298 K. Calculate (a) the number of collisions against the vessel walls within 1 s/cm^2 , (b) the number of collisions between molecules within 1 cm^3 per second, and (c) the mean free path length for nitrogen molecules.

2. The thermal decomposition of gaseous acetaldehyde is a bimolecular reaction. Its activation energy E is $1911 \times 10^3 \text{ J/mole}$, and the molecular diameter of acetaldehyde is $5 \times 10^{-8} \text{ cm}$. Calculate the number of molecules reacting within $1 \times 10^{-6} \text{ m}^3$ per second at 800 K and $1.01 \times 10^5 \text{ Pa}$ and compare the result with the experimental value of 7.3×10^{16} . Also determine the half-life of acetaldehyde in this reaction.

3. The thermal decomposition of nitrogen dioxide, $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$, is a homogeneous bimolecular reaction. At 627 K, the reaction rate constant is $1.84 \times 10^3 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. The steric factor is 0.019. Calculate the activation energy E , assuming that the molecular diameter of NO_2 is $3.55 \times 10^{-8} \text{ cm}$. Determine the fraction of the molecules whose energy at 627 K exceeds E .

4. The rate constant of the azoisopropane dissociation reaction $\text{C}_3\text{H}_7\text{N}=\text{NC}_3\text{H}_7 \rightarrow \text{N}_2 + \text{C}_3\text{H}_{14}$ is given by the equation $k_1 = 5.71 \times 10^{13} e^{-40900/RT}$. Calculate the maximum possible value, from the standpoint of the collision theory, of the pre-exponential factor, assuming that $\sigma_{\text{C}_3\text{H}_7\text{N}=\text{NC}_3\text{H}_7} = 5 \times 10^{-8} \text{ cm}$, $c_{\text{C}_3\text{H}_7\text{N}=\text{NC}_3\text{H}_7} = 1 \text{ mole per 22.4 litre}$, and $T = 563 \text{ K}$. Compare the result with the experimental values.

5. The activation energy of the acetone dissociation reaction $\text{CH}_3\text{COCH}_3 = \text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$ is 286.6 kJ/mole . Assuming that the molecular diameter of acetone is $5.0 \times 10^{-8} \text{ cm}$, calculate the rate constant of this reaction at 835 K and 760 mm Hg. Compare the result with the experimental value $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$.

6. The experimental value of the rate constant of the reaction between methyl iodide and sodium ethylate, $\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{NaI}$, proceeding in an ethanol solution at 291 K, is $4.96 \times 10^{-4} \text{ litre mole}^{-1} \text{ s}^{-1}$. Assuming that the molecular radii are 2.64×10^{-8} and $2.74 \times 10^{-8} \text{ cm}$, respectively, calculate the activation energy of this reaction, using the equation from the collision theory ($p = 0.8$).

7. The value of k_0 in the Arrhenius equation

$$k_0 = 1.6 \times 10^{11} e^{-E/RT}$$

for the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ is known. Calculate the steric factor p and activation energy E and compare the results with the tabulated values ($p = 0.14$, $E = 162.758 \text{ kJ/mole}$) if, at 700 K, the mean rate constant is $6.4 \times 10^{-2} \text{ litre mole}^{-1} \text{ s}^{-1}$ and the viscosities are $\eta_{\text{H}_2} = 1.83 \times 10^{-3} \text{ Pa s}$ and $\eta_{\text{I}_2} = 3.6 \times 10^{-3} \text{ Pa s}$.

8. The kinetics of the reaction between triethylamine and ethyl bromide in benzene, $(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{Br} \rightarrow$, was studied with the following results:

T, K	273.12	283.2	293.2	303.2
$k \times 10^3, \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$	0.28	0.558	1.17	2.22

The reaction is irreversible and of the second order. Calculate its activation energy and steric factor if the densities of the reactants are $d_{(\text{C}_2\text{H}_5)_3\text{N}} = 0.723 \text{ g/cm}^3$ and $d_{\text{C}_2\text{H}_5\text{Br}} = 1.456 \text{ g/cm}^3$.

9. The kinetics of the reaction between dimethylbenzylamine and methyl iodide in nitrobenzene, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{N} + \text{CH}_3\text{I} \rightarrow$, was studied with the following results:

T, K	273.2	283.2	293.3	303
$k \times 10^3, \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$	0.922	1.64	4.615	9.65

The reaction is irreversible and of the second order. Calculate its activation energy and steric factor if the densities of the reactants are $d_a = 0.956 \text{ g/cm}^3$ and $d_{\text{m.i.}} = 2.28 \text{ g/cm}^3$.

10. The kinetics of the reaction between ethyl iodide and dimethylbenzylamine in acetone, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \text{C}_2\text{H}_5\text{I} \rightarrow$, was studied with the following results:

T, K	273.2	283.2	293.2	303.2
$k \times 10^3, \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$	0.27	0.677	1.518	3.398

The reaction is irreversible and of the second order. Calculate its activation energy and steric factor if $d_a = 0.956 \text{ g/cm}^3$ and $d_{\text{m.i.}} = 1.933 \text{ g/cm}^3$.

11. Calculate the sum over states for the linear activated complex $\text{H} \cdots \text{H} \cdots \text{Br}$ if (a) the $\text{H} \cdots \text{H}$ distance is $1.50 \times 10^{-8} \text{ cm}$ and the $\text{H} \cdots \text{Br}$ distance is $1.42 \times 10^{-8} \text{ cm}$, and (b) the vibrational frequencies of the molecule are 2340, 460, and 460 cm^{-1} (the fourth frequency corresponds to the vibration along the barrier and is not required for the calculation).

12. Proceeding from the theory of absolute reaction rates, determine the temperature dependence of the pre-exponential factor for the following types of reactions: (a) bimolecular reaction between an atom and a diatomic molecule, yielding a linear activated complex, and (b) trimolecular reaction between two atoms and a diatomic molecule, yielding a nonlinear activated complex lacking degrees of freedom. The vibrational sum over states is independent of temperature.

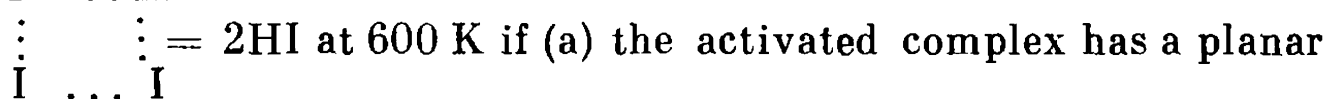
13. The following parameters are known for the elementary reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$: (a) the difference between the zeroth energy levels in the activated and initial states is 62,76 J; (b) the molecular configuration: $\text{O}_2 r_{\text{O-O}} = 0.12 \text{ nm}$; the activated complex H-O-O is linear with $r_{\text{H-O}} = 0.1 \text{ nm}$ and $r_{\text{O-O}} = 0.14 \text{ nm}$; (c) the vibrational

frequency for O_2 is $\nu = 1580 \text{ cm}^{-1}$, and for $H-O-O$ there are no stretching vibrations except for the doubly degenerate bending vibration at $\nu = 300 \text{ cm}^{-1}$; and (d) the barrier factor is $\kappa = 1$. The electronic sums over states are disregarded. Calculate the reaction rate constant at 800 K.

14. The following parameters are known for the reaction $H + HCl = H_2 + Cl$: (a) the difference between the zeroth energy levels in the initial and activated states is 18.828 kJ; (b) the molecular configuration: $r_{H-H} = 0.13 \text{ nm}$; (c) all vibrational frequencies are sufficiently high and $Q_{\text{vibr}} = 1$; and (d) the barrier factor is $\kappa = 1$. The electronic sums over states are ignored. Calculate the reaction rate constant at 600 K.

15. The following parameters are known for the reaction $O + OC \rightarrow O \cdots C \cdots O \rightarrow CO_2$: (a) the difference between the zeroth energy levels in the initial and activated states is 83.68 kJ; (b) the molecular configuration: CO , $r_{C-O} = 0.112 \text{ nm}$; the activated complex, $r_{O-C-O} = 0.12 \text{ nm}$, is linear with known dimensions; (c) all vibrational frequencies are sufficiently high ($Q_{\text{vibr}} = 1$) except for the doubly degenerate bending vibration of the activated complex at $\nu = 200 \text{ cm}^{-1}$; and (d) the barrier factor is $\kappa = 1$. The electronic sums over states are disregarded. Calculate the rate constant of this reaction at 500 K.

16. Calculate the rate constant of the reaction $H_2 + I_2 = H \cdots H$



structure and its three principal moments of inertia are, respectively, $I_A = 920 \times 10^{-40} \text{ g cm}^2$, $I_B = 7 \times 10^{-40} \text{ g cm}^2$, and $I_C = 930 \times 10^{-40} \text{ g cm}^2$; (b) $r_{H-H} = 0.07 \text{ nm}$ and $r_{I-I} = 0.25 \text{ nm}$; (c) for all vibrational degrees of freedom, $Q_{\text{vibr}} = 1$, except for one vibration in the activated complex at $\nu = 100 \text{ cm}^{-1}$; (d) the barrier factor is $\kappa = 1$, and the electronic sums over states are disregarded; and (e) the activation energy is $E = 167.36 \text{ kJ/mole}$.

17. Two reactions of the same order have equivalent activation energies but the entropies of their activation differ by $42 \text{ J mole}^{-1} \text{ K}^{-1}$. Calculate the ratios of their rate constants at 300 K.

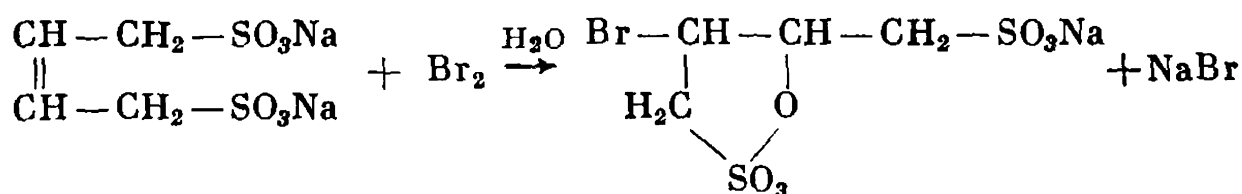
18. Calculate the rate constant of dimerization of ethylene, $2C_2H_4 \rightarrow C_4H_8$, at 673 K if, for 1-butene, $\Delta H^\ddagger = 147\,466 \text{ J/mole}$ and $\Delta S^\ddagger = -147 \text{ J mole}^{-1} \text{ K}^{-1}$.

19. For the reaction between pyridine and ethyl iodide,



at 303 K, $k = 1.72 \times 10^{-6} \text{ litre mole}^{-1} \text{ s}^{-1}$ and $\Delta S^\ddagger = -118.5 \text{ J mole}^{-1} \text{ K}^{-1}$. Calculate the heat of activation (ΔH^\ddagger) and the activation energy E .

20. Calculate the heat of activation and activation energy for the reaction of bromination of 2-butene-1,4-disulphonate,



at 298 K, proceeding from the following data:

$T, \text{ K}$	293	298	303
$k \times 10^{-3}, \text{ min}^{-1}$	8.9	11.0	13.7

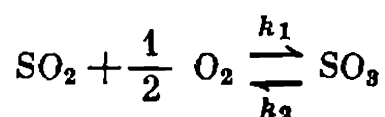
if the conversion factor is unity and ΔS^\ddagger and ΔH^\ddagger are independent of temperature.

21. The rate constant k of the reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ is 6.63×10^5 mole/litre at 600 K and 6.52×10^5 mole/litre at 645 K. At the same temperatures, k for the backward reaction is 83.9 and 407, respectively. Calculate (a) the equilibrium constants for these temperatures, (b) the activation energy E of the forward and backward reactions, and (c) the heat of activation (ΔH^\ddagger) of the forward and backward reactions.

22. The rate constants of the nitrogen oxide dissociation reaction $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$ are $k_1 = 0.0108$ mole litre⁻¹ s⁻¹ atm⁻² at $T_1 = 1620$ K and $k_2 = 0.0030$ mole litre⁻¹ s⁻¹ atm⁻² at $T_2 = 1525$ K. Calculate ΔH^\ddagger and ΔS^\ddagger at the mean temperature of 1527 K, using the equation from the theory of absolute reaction rates.

23. In the case of homogeneous first-order reactions between gases, the entropy of activation is often insignificant and can be ignored. Assuming that $\Delta S^\ddagger = 0$, determine the rate constant and the time of transformation of a substance by half at room temperature (300 K) if the heat of activation of the reaction is (a) 63×10^3 J/mole, (b) 84×10^3 J/mole, and (c) 105×10^3 J/mole.

24. The rate of the reaction



was studied, and the following rate constants of the forward and backward reactions were obtained at different temperatures:

$T, \text{ K}$	873	879	898	933	938	947
$k_1, \text{ min}^{-1}$	82.5	92.0	132.0	196.0	209.0	279.0
$k_2, \text{ min}^{-1}$	9.95	11.8	23.8	52.3	58.25	85.6

Calculate the heat and entropy of activation for the forward and backward reactions. Check whether the theory of transition state is applicable within this temperature range.

25. Determine the rate constant of ethylene dimerization $2\text{C}_2\text{H}_4 \rightarrow \text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_3$ at 300 K if the standard entropies of ethylene and the activated complex (at $P = 1$ atm), determined by the translational, rotational, and vibrational motions of the molecules, are as tabulated below:

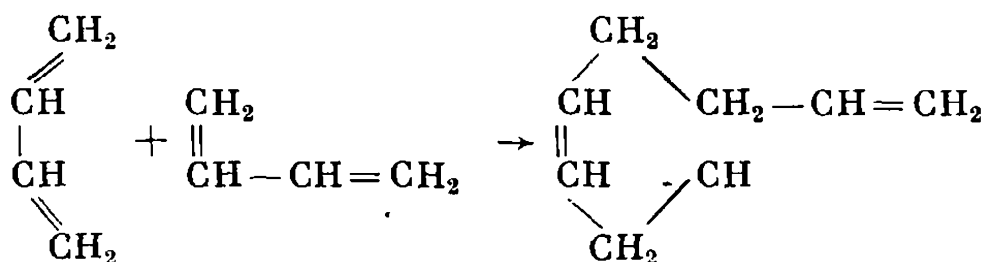
Substance	Entropy, J mole ⁻¹ K ⁻¹			ΔS^\ddagger , J mole ⁻¹ K ⁻¹	
	S_{trans}^0	S_{rot}^0	S_{vibr}^0	$P = \text{const}$	$V = \text{const}$
$2\text{C}_2\text{H}_4$	302.63	132.92	5.52	-125.82	
C_4H_8	160.094	136.69	18.39		-41.80

The experimentally found activation energy is 146.30 kJ.

26. The frequency factor of the dissociation of dimeric cyclopentadiene in the gas phase is $1.3 \times 10^{13} \text{ s}^{-1}$, and the activation energy of the process is 146.30 kJ. Calculate (a) the rate constant at 373 K and (b) the entropy of activation.

27. The rate constant of sulphamic acid hydrolysis is $1.16 \times 10^{-3} \text{ litre mole}^{-1} \text{ s}^{-1}$ at 363 K, and the activation energy is 127.49 kJ/mole. Calculate ΔA^\ddagger , ΔH^\ddagger , and ΔS^\ddagger for the hydrolysis reaction.

28. A reaction between two butadiene molecules yields 3-vinylcyclohexane:



It is assumed that the structure of the activated complex is that of a biradical $\dot{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ which closes into a ring through linking of two free valences. Calculate the rate constant of butadiene dimerization, in $\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$, at 600 K if the experimentally found activation energy is 99.024 kJ/mole. The standard entropies are tabulated below.

Substance	Entropy, J mole ⁻¹ K ⁻¹			ΔS^\ddagger , J mole ⁻¹ K ⁻¹	
	S_{trans}^0	S_{rot}^0	S_{vibr}^0	$P = \text{const}$	$V = \text{const}$
$2\text{C}_4\text{H}_6$	339.42	270.86	132.09	-119.13	-71.06
C_8H_{12}	182.67	214.85	183.92		

29. Demonstrate that the entropy term involved in the calculation of the rate of ethylene dimerization $2\text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_8$ has a value close to that of the steric factor in the collision theory. The experimentally found activation energy is 146.30 kJ/mole, the effective diameter of the ethylene molecule at 300 K is $\sigma = 4.9 \times 10^{-8}$ cm, and the experimental value of the dimerization rate constant is $k = 1.08 \times 10^{-14}$ cm³ mole⁻¹ s⁻¹. The standard entropies of ethylene and the activated complex at pressures equal to unity are tabulated below.

Substance	Entropy, J mole ⁻¹ K ⁻¹			ΔS^\ddagger , J mole ⁻¹ K ⁻¹	
	S_{trans}^0	S_{rot}^0	S_{vibr}^0	$P = \text{const}$	$V = \text{const}$
$2\text{C}_2\text{H}_4$	302.63	132.92	5.52	-125.82	-41.80
C_4H_8	139.20	136.69	18.39		

30. Calculate the rate constant of the reaction of recombination of methyl radicals at 473 K (second-order reaction) if the activation energy is zero, (a) the collision diameter being 2.03×10^{-8} cm according to the theory of collision of inelastic spheres and (b) the entropy of activation being 8.4 J mole⁻¹ K⁻¹ according to the theory of absolute reaction rates. Assume that the standard state corresponds to 1 mole/cm³.

31. The reaction $\text{A} + \text{B} + \text{C} \rightarrow \text{D}$ comprises the following steps:



Step (I) is a reversible reaction. Demonstrate that the temperature dependence of the rate constant is given by the equation

$$k = k_0 e^{-(E_a + \Delta H)/RT}$$

in which ΔH is the change in enthalpy during step (I).

Multivariate Problems

1. A chemical reaction proceeds under conditions given in the table on pp. 438-439. Determine, from the collision theory, the kinetic characteristic of the reaction, which is absent in a given variant.

2. Determine the activation energy E_a of a reaction whose rate constant k is known from experimental data at T , K, and a partial pressure of 1.01×10^5 Pa. The steric factor is assumed to equal unity. Compare the found activation energy and molecular diameter

Variant	Reaction	T, K	Rate constant, k	Activation energy E_a , kJ/mole	Steric factor p	Diameter of reacting particles d_{mean} , cm	Answer
1	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	627	$1.81 \times 10^3 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$	111.2	0.019	?	$3.12 \times 10^{-8} \text{ cm}$
2	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	700	?	165.44	0.47	2.0×10^{-8} 2.0×10^{-8}	$70.24 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
3	$\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{OC}_2\text{H}_5$ + NaI in ethanol	291	$4.96 \times 10^{-4} \text{ litre mole}^{-1} \text{ s}^{-1}$?	0.8	2.64×10^{-8} 2.74×10^{-8}	80.75 kJ
4	$\text{CH}_3\text{COCH}_3 = \text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$, $P = 760 \text{ mm Hg}$	835	?	286.3	3.4×10^{-5}	5.0×10^{-8}	$5.21 \times 10^{-9} \text{ s}^{-1}$
5	$\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$, $P = 550 \text{ mm Hg}$	1050	$0.54 \times 10^{-3} \text{ s}^{-1}$?	2×10^{-5}	4.5×10^{-8}	255.96 kJ
6	$\text{C}_2\text{H}_5\text{Br} + (\text{C}_2\text{H}_5)_3\text{N} \rightarrow (\text{C}_2\text{H}_5)_4\text{NBr}$ in acetone	333	?	50.32	4.9×10^{-8}	5×10^{-8} 5×10^{-8}	
7	$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	787	$1.77 \times 10^{-2} \text{ litre mole}^{-1} \text{ s}^{-1}$?	0.05	2.0×10^{-8} 2.0×10^{-8}	177.6 kJ
8	$\text{CH}_3\text{NNCH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{N}_2$, $P = 487 \text{ mm Hg}$	603	$2.96 \times 10^{-3} \text{ min}^{-1}$	219.199	?	3.98×10^{-8}	$p = 14.2 \times 10^6$

(Table concluded)

Variant	Reaction	T, K	Rate constant, k	Activation energy E_a , kJ/mole	Steric factor p	Diameter of reacting particles, cm	Answer
9	$\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2$, $P = 810 \text{ mm Hg}$	1085	$5.7 \times 10^{-4} \text{ s}^{-1}$?	1	3.3×10^{-8}	256.75 kJ
10	$\text{C}_3\text{H}_7\text{I} + (\text{CH}_3)_2\text{NH} \rightarrow (\text{CH}_3)_2\text{C}_3\text{H}_7\text{NHI}$ in ethanol	333	$2.75 \times 10^{-3} \text{ litre mole}^{-1} \text{ s}^{-1}$	629.93	2.5×10^{-6}	$\sigma_1 = \sigma_2$	$7.84 \times 10^{-8} \text{ cm}$
11	$2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$	1440.2	?	100.32	1	3.5×10^{-8}	$3.47 \times 10^{-7} \text{ litre mole}^{-1} \text{ s}^{-1}$
12	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	627	$1.81 \times 10^3 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$?	0.019	3.55×10^{-8}	127.63 kJ
13	$2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$	384	?	91.86	1	4.8×10^{-8}	$93.43 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
14	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	716	?	186.43	1	3.5×10^{-8}	$2.50 \times 10^{-3} \text{ litre mole}^{-1} \text{ s}^{-1}$
15	$\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$	552.3	$2.742 \times 10^{-3} \text{ min}^{-1}$?	1	3.8×10^{-8}	—
16	$\text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H}_3$	277.5	$2.19 \times 10^{-4} \text{ cm molecule}^{-1} \text{ s}^{-1}$?	4.47×10^{-4}	2.72×10^{-8}	—
17	$\text{CH}_3\text{CO} - \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$, $P = 760 \text{ mm Hg}$	835	$1.5 \times 10^{-3} \text{ s}^{-1}$	286.33	3.48×10^{-6}	?	$5 \times 10^{-8} \text{ cm}$

with the values given in handbooks. (Assume that the diameter of the atoms equals that of the molecule, the molecular diameter being determined from critical and kinetic data.)

Variant	Reaction	T, K	k
1	$\text{H} + \text{HD} \rightarrow \text{HD} + \text{H}$	1000.2	$0.68 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
2	$\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$	1000.2	$0.95 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
3	$\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$	1000.2	$1.2 \times 10^{-12} \text{ litre s}^{-1} \text{ mole}^{-1}$
4	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	647.2	$0.0140 \text{ litre min}^{-1} \text{ mole}^{-1}$
5	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	629.2	$0.00676 \text{ litre min}^{-1} \text{ mole}^{-1}$
6	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	847.7	$8.56 \times 10^2 \text{ litre min}^{-1} \text{ mole}^{-1}$
7	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	771.2	$3.6 \times 10^{-4} \text{ litre min}^{-1} \text{ mole}^{-1}$
8	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	829.2	$2.11 \times 10^{-5} \text{ litre min}^{-1} \text{ mole}^{-1}$
9	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	556.2	$0.942 \times 10^{-6} \text{ litre min}^{-1} \text{ mole}^{-1}$
10	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	666.2	$0.588 \times 10^{-3} \text{ litre min}^{-1} \text{ mole}^{-1}$
11	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	683.2	$0.00137 \text{ litre min}^{-1} \text{ mole}^{-1}$
12	$\text{D} + \text{HD} \rightarrow \text{DH} + \text{D}$	1000.2	$1.0 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
13	$\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$	1000.2	$2.5 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
14	$\text{D} + \text{DH} \rightarrow \text{D}_2 + \text{H}$	1000.2	$0.79 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
15	$\text{T} + \text{H}_2 \rightarrow \text{HT} + \text{H}$	1000.2	$2.2 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
16	$\text{T} + \text{D}_2 \rightarrow \text{DT} + \text{D}$	1000.2	$1.2 \times 10^{-9} \text{ litre s}^{-1} \text{ mole}^{-1}$
17	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1893.2	$19.18 \times 10^{-1} \text{ litre s}^{-1} \text{ mole}^{-1}$
18	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1628.2	$38.43 \times 10^1 \text{ litre s}^{-1} \text{ mole}^{-1}$
19	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1473.2	$62.46 \times 10^3 \text{ litre s}^{-1} \text{ mole}^{-1}$
20	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1235.2	$39.82 \times 10^3 \text{ litre s}^{-1} \text{ mole}^{-1}$
21	$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	1259.2	$6.72 \times 10^3 \text{ litre s}^{-1} \text{ mole}^{-1}$
22	$\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$	571.2	$2.03 \times 10^{-3} \text{ litre min}^{-1} \text{ mole}^{-1}$
23	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$	611.4	$286 \times 10^{-3} \text{ litre min}^{-1} \text{ mole}^{-1}$
24	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$	581.4	$7.9 \text{ litre min}^{-1} \text{ mole}^{-1}$
25	$2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$	1351.2	$110.9 \times 10^3 \text{ litre min}^{-1} \text{ mole}^{-1}$
26	$2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$	1441.2	$977.0 \text{ litre min}^{-1} \text{ mole}^{-1}$

3. The rate constants of an n th-order reaction (A) have been determined at different temperatures. (For the reaction with $n = 1$, k is given in s^{-1} , and with $n = 2$, k is given in $\text{cm}^3 \text{s}^{-1} \text{mole}^{-1}$.) Calculate (a) the activation energy, (b) the pre-exponential factor, (c) the heat of activation, (d) the entropy of activation, and (e) the temperature coefficient of the reaction rate.

Variant	Reaction (A)	T, K	k
1	Hydrolysis of $(\text{CH}_2)_6\text{C} \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$ in 80% ethanol, $n=1$	273	1.06×10^{-5}
		298	3.19×10^{-4}
		308	9.86×10^{-4}
		318	2.92×10^{-3}
2	$\text{N}_2\text{O} \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$, $n=1$	273.1	7.87×10^{-7}
		288.1	1.05×10^{-5}
		283.1	1.76×10^{-5}
		298.1	3.38×10^{-5}
		308.1	1.35×10^{-4}
		313.1	2.47×10^{-4}
		318.1	4.98×10^{-4}
		323.1	7.59×10^{-4}
		328.1	1.50×10^{-3}
		338.1	4.87×10^{-3}
3	Dissociation of acetodicarboxylic acid in an aqueous solution, $n=1$	273.2	2.46×10^{-5}
		293.2	47.5×10^{-5}
		333.2	5.480×10^{-5}
		273.2	7.67×10^{-7}
4	$\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$, $n=1$	298.2	3.46×10^{-5}
		308.2	1.46×10^{-4}
		318.2	4.98×10^{-4}
		328.2	1.50×10^{-3}
5	$\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$	338.2	4.87×10^{-3}
		750	4.539×10^{-3}
		760	7.194×10^{-3}
		770	1.125×10^{-2}
		780	1.741×10^{-2}
		790	2.667×10^{-2}
6	$\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$, $n=1$	800	4.140×10^{-2}
		300	3.288×10^6
		310	6.652×10^6
		320	1.259×10^7
		330	2.398×10^7
		340	4.295×10^7
		350	7.447×10^7
7	$\text{cyclo}-(\text{CH}_3\text{CHO})_2 \rightarrow 3\text{CH}_3\text{CHO}$, $n=1$	500	5.175×10^{-5}
		510	1.238×10^{-4}
		520	2.345×10^{-4}

(Table continued)

Variant	Reaction (A)	T, K	k
7	$\text{cyclo}-(\text{CH}_3\text{CHO})_2 \rightarrow 3\text{CH}_3\text{CHO}, n=1$	530	6.455×10^{-4}
		540	1.404×10^{-3}
		550	2.994×10^{-3}
8	$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CHBrCH}_3, n=2$	300	7.638×10^{-7}
		310	2.055×10^{-6}
		320	6.309×10^{-6}
		330	1.888×10^{-5}
		340	5.188×10^{-5}
		350	5.902×10^{-4}
		360	3.020×10^{-4}
9	$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6, n=2$	600	7.413×10^{-3}
		610	1.343×10^{-2}
		620	2.38×10^{-2}
		630	4.149×10^{-2}
		640	7.145×10^{-2}
		650	7.586×10^{-1}
		660	1.995×10^{-1}
10	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}, n=2$	500	7.834×10^{-4}
		510	1.714×10^{-3}
		520	0.243×10^{-3}
		530	7.48×10^{-3}
		540	1.503×10^{-2}
		550	2.930×10^{-2}
		560	5.610×10^{-2}
11	$\text{HI} + \text{CH}_3\text{I} \rightarrow \text{CH}_4 + \text{I}_2, n=2$	400	9.954×10^{-5}
		410	2.780×10^{-4}
		420	7.396×10^{-4}
		430	1.884×10^{-3}
		440	4.592×10^{-3}
		450	5.370×10^{-3}
		460	2.427×10^{-2}
12	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2, n=2$	500	2.938×10^{-6}
		510	7.096×10^{-6}
		520	1.652×10^{-5}
		530	3.732×10^{-5}
		540	8.185×10^{-5}
		550	1.742×10^{-4}
		560	3.606×10^{-4}

(Table concluded)

Variant	Reaction (A)	T, K	k
13	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2, n = 2$	350	1.119×10^{-4}
		360	4.130×10^{-4}
		370	1.119×10^{-3}
		380	2.999×10^{-3}
		390	7.499×10^{-3}
		400	1.786×10^{-2}
		410	4.083×10^{-2}
14	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH},$ $n = 2$ (solvent: H_2O)	280	24.378
		290	48.865
		300	93.540
		310	122.460
		320	216.272
		330	369.828
15	$\text{CH}_3\text{Br} + \text{NaI} \rightarrow \text{CH}_3\text{I} + \text{NaBr}, n = 2$ (solvent: H_2O)	280	8.395×10^{-2}
		290	2.075×10^{-1}
		300	7.55×10^{-1}
		310	2.032
		320	5.152
		330	1.233
16	$2\text{H}_2\text{C} = \text{HC} - \text{HC} = \text{CH}_2$ $\rightarrow \text{CH}_2 = \text{C} \begin{array}{l} \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \text{CH}_2 - \text{CH} = \text{CH}_2 \end{array}, n = 2$	503	0.531
		513	0.751
		523	1.19
		527	1.40
		530	1.70
		540	2.43
		555	4.18
		578	9.85
		606	25.4
		622	44.5
		642	84.4
		973	0.14×10^{-4}
		1023	0.28×10^{-4}
		1073	0.14×10^{-3}
17	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2, n = 2$	1221	0.012
		1273	0.018
		1323	0.024

CHAPTER 25

Kinetics of Photochemical
and Chain Reactions

Basic Equations and Symbols

The relationship between the intensity of the luminous flux passing through a solution layer having a thickness l and the number n of molecules of the medium is given by the Lambert-Beer law

$$I = I_0 e^{-knl} \quad (25.1)$$

where I is the luminous flux intensity after absorption in a solution layer l cm thick, I_0 is the intensity of the luminous flux before it passes through the absorbing layer, k is the molecular absorption coefficient, and n is the number of absorbing molecules per cubic centimetre.

The energy absorbed by a medium is given by van't Hoff's law

$$E = I_0 (I - e^{-knl}) \quad (25.2)$$

where E is the energy absorbed per unit time.

A quantitative characteristic of photochemical reactions is the quantum yield γ of the reaction, that is the number of reactant molecules per absorbed quantum of luminous flux (Stark-Einstein law):

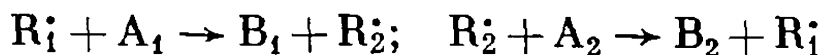
$$\gamma = n_r/n_a \quad (25.3)$$

where γ is the quantum yield, n_r is the number of molecules per unit volume, which have reacted as a result of absorption of luminous flux quantum per unit time, and n_a is the number of luminous flux quanta absorbed per unit time within 1 cm³ of solution; $n_a = E/h\nu$.

The kinetic equation for a photochemical reaction is

$$-\frac{dn}{dt} = \gamma \frac{I_0}{h\nu} (1 - e^{-knl}) \quad (25.4)$$

The rate of a chain reaction with respect to any component equals the rate of that chain propagation step in which the component in question is formed or spent. For example, if a chain link involves two elementary reactions with the reactants being spent and reaction products formed in each:



where R_i^\cdot stands for free radicals, then the rate of an unbranched chain reaction is given by the equation

$$\begin{aligned} -\frac{d[A_1]}{dt} &= \frac{d[B_1]}{dt} = k_1 [R_1^\cdot] [A_1] \\ -\frac{d[A_2]}{dt} &= \frac{d[B_2]}{dt} = k_2 [R_2^\cdot] [A_2] \end{aligned} \quad (25.5)$$

While writing the differential equations for the concentrations of free radicals, one must take into account the rates of the chain initiation and termination processes. As a rule, chain initiation results in formation of one of the free radicals participating in the chain reaction, for instance, R_1^\cdot . If the free radical formation rate is denoted by w_0 and the rates of free radical degradation are denoted by w_{d_1} and w_{d_2} , we have the following equations:

$$\frac{d[R_1^\cdot]}{dt} = w_0 - k_1 [R_1^\cdot] [A_1] + k_2 [R_2^\cdot] [A_2] - w_{d_1} \quad (25.6)$$

and

$$\frac{d[R_2^\cdot]}{dt} = k_1 [R_1^\cdot] [A_1] - k_2 [R_2^\cdot] [A_2] - w_{d_2} \quad (25.7)$$

in which w_0 is a function of concentration of the initial substances or some initiators and is independent of the free radical concentrations, and w_{d_1} and w_{d_2} are functions of free radical concentrations. Since free radicals are highly active intermediate particles, their concentration may be considered steady-state almost throughout the process; that is

$$w_0 = w_{d_1} + w_{d_2} \quad (25.8)$$

Under steady-state conditions, the rate of chain initiation is equal to that of chain termination. If it is assumed that the chain termination occurs only at one of the free radicals, then Eq. (25.8) takes the form

$$w_0 = w_d \quad (25.9)$$

In the case of linear chain termination,

$$w_0 = k_3 [R_i] \quad (25.10)$$

The rate of an unbranched chain reaction will be

$$w = k_i (w_0/k_3) [A_i]$$

in the case of linear chain termination and

$$w_0 = 2k_3 [R_i]^2 \quad (25.11)$$

and

$$w = k_i \sqrt{w_0/2k_3} [A_i]$$

in the case of quadratic chain termination, k_3 being the chain termination rate constant.

The chain propagation step involving the free radical at which the main chain termination takes place is limiting for the chain link, and the subscript i relates to the limiting step of chain propagation. The chain length ν in an unbranched chain reaction equals the chain reaction rate divided by that of chain termination (or initiation).

Therefore,

$$v = (k_i/k_3) [A_i] \quad (25.12)$$

in the case of linear chain termination and

$$v = \frac{k_i}{\sqrt{2k_3w_0}} [A_i] \quad (25.13)$$

in the case of quadratic chain termination.

The order of chain reactions with respect to their individual components and the effective rate constant can be determined from the kinetics of accumulation of the reaction products or consumption of the initial substances. The effective rate constant is essentially a combination of those of chain initiation, propagation, and termination. The temperature dependence of the effective rate constant is given by the Arrhenius equation. In the case of linear chain termination, the measured effective activation energy is expressed as

$$E_{\text{eff}} = E_0 + E_1 - E_3 \quad (25.14)$$

where E_0 is the activation energy of chain initiation, E_1 is that of the chain propagation reaction involving a less active free radical, and E_3 is the activation energy of chain termination. Similarly, in the case of quadratic chain termination,

$$E_{\text{eff}} = \frac{1}{2} E_0 + E_1 - \frac{1}{2} E_3 \quad (25.15)$$

The rate of a branched chain reaction can be written as

$$\frac{dn}{dt} = w_0 + \varphi n \quad (25.16)$$

where n is the total concentration of free valences, w_0 is the chain initiation rate, and φ is the difference between the rates of chain branching and termination. If both processes are of the first order with respect to the free radical concentration, the rates can be expressed as fn and qn . Then,

$$\frac{dn}{dt} = w_0 - (q - f) n \quad (25.17)$$

Written in this form, Eq. (25.17) corresponds to chain branching reactions. If $q > f$, a steady-state concentration of free radicals is established in the system:

$$n = w_0/(q - f) \quad (25.18)$$

The occurrence of the chain branching reaction merely increases the steady-state concentration, which is equivalent to a decrease in the chain termination rate at $f = 0$. Then, a steady-state reaction oc-

curs in the system, whose kinetics is basically the same as for unbranched chain reactions. If $f > q$ and $f - q = \varphi > 0$, integration of Eq. (25.16) gives

$$n = \frac{w_0}{\varphi} (e^{\varphi t} - 1) \quad (25.19)$$

or, at $\varphi t > 1$,

$$n = \frac{n_0}{\varphi} e^{\varphi t} = A e^{\varphi t} \quad (25.20)$$

As can be inferred from Eq. (25.20), the free radical concentration progressively increases, just as the chain reaction rate. Every $1/\varphi$ s, the free radical concentration and, consequently, the chain reaction rate increases by a factor of e , and within a time period equal to several $1/\varphi$ explosive reactions take place where none were observed. Chain branching reactions are characterized by two clearly defined sets of conditions. If the chain termination rate exceeds that of chain branching, the process takes a steady-state course and its rate is immeasurably small. If the chain termination rate is less than the rate of branching, we are dealing with an unsteady self-accelerating process at the end of which the mixture undergoes chain combustion. Transition from the condition $q > f$ to $f > q$ may take place if slight change occurs in one of the parameters determining the rate of chain termination or branching, such as pressure, temperature, composition of the mixture, size of the reaction vessel, and the state of its walls. Thus, a slight change in one of the above parameters may cause a slow steady-state reaction to become a fast explosive process and vice versa. Such phenomena in chemical kinetics are referred to as limiting or critical. The value of the parameter triggering the transition from one set of conditions to the other is known as the inflammation limit.

Exercises

1. Proceeding from the following data, determine the quantum yield of uranyl oxalate dissociation for each wavelength:

Wavelength, nm	Fraction of dissociated oxalate	Number of dissociated molecules $\times 10^{-18}$	Number of absorbed photons $\times 10^{-18}$
365.5	0.0592	6.18	10.58
365.5	0.0498	4.32	8.93
435.8	0.0242	2.10	3.64
435.8	0.0208	1.79	3.10

Solution. Calculate the quantum yield at 365.3 nm, using Eq. (25.3)

$$\gamma = \frac{\text{number of dissociated molecules}}{\text{number of absorbed photons}} = \frac{5.18 \times 10^{18}}{10.58 \times 10^{18}} = 0.490$$

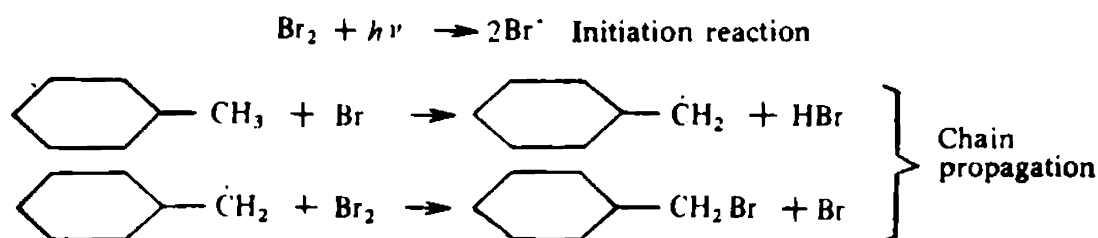
For the rest of measurements, γ equals 0.490, 0.483, 0.576, and 0.577, respectively.

2. The photochemical bromination of toluene proceeds according to the following overall equation:

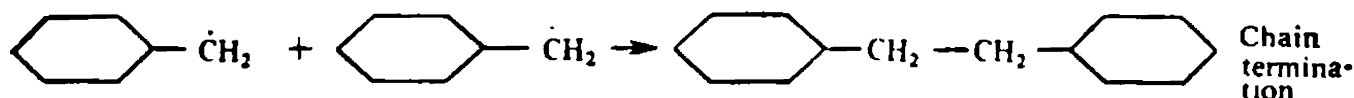


The reaction is based on a chain mechanism, as suggested by the high quantum yield. Represent schematically the chain reaction mechanism if the chain terminates at the free benzyl radical and free radicals result from photochemical decomposition of Br_2 . Write the stoichiometric equation of the chain reaction if the chain length is ν . Determine the number of Br_2 and $\text{C}_6\text{H}_5\text{CH}_3$ molecules spent in the reaction and that of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, HBr , and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ molecules forming within a chain if its length is $\nu = 50$.

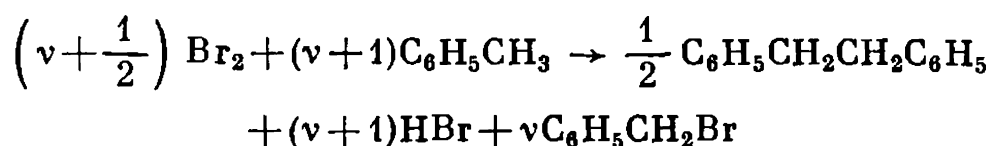
Solution. Chain reactions are composite ones and, strictly speaking, they cannot be described by a single stoichiometric equation. The reason is that chain termination often gives rise to some side substances. The toluene bromination reaction proceeds according to the following mechanism:



According to the statement of the problem, the chain terminates at the benzyl radical:

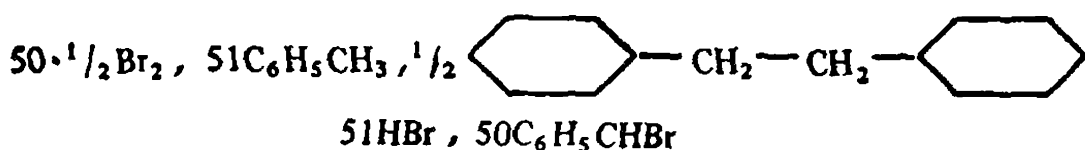


Since the chain length is ν , the $(\nu + 1)$ link will be incomplete. As a result, a toluene molecule will be spent in the last link, an HBr molecule will be formed, but no benzyl bromide will be formed, and no Br_2 molecule will be spent. If it is also borne in mind that half of the Br_2 molecule was spent in the course of chain initiation, the complete equation of the process can be written as



This expression can be regarded as the stoichiometric equation of the chain reaction. In contrast with ordinary stoichiometric equations, the quantity ν depends on the reaction conditions.

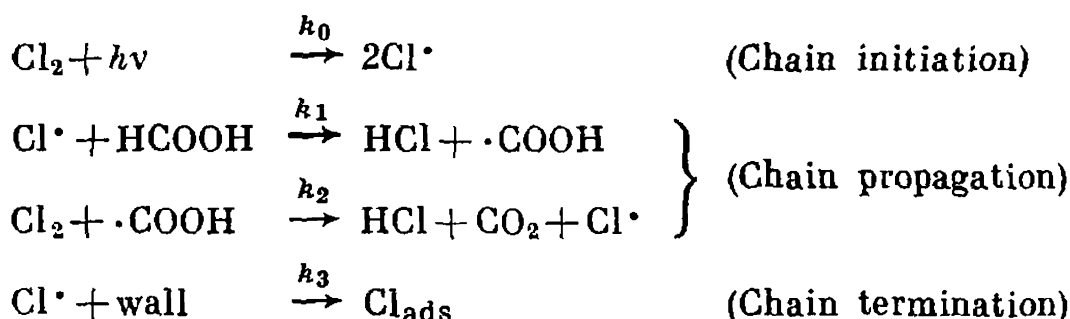
Determine the number of molecules formed and spent at $\nu = 50$:



3. The kinetics of photochemical chlorination of formic acid in the gas phase is given by the differential equation

$$-\frac{d[\text{Cl}_2]}{dt} = k[\text{Cl}_2][\text{HCOOH}]$$

We are dealing here with a chain reaction, which is indicated by the high quantum efficiency. Derive the differential equation for the following reaction:



Solution. To determine the rate of this chain reaction use the formula

$$w = k_i \frac{w_0}{k_3} [A_i]$$

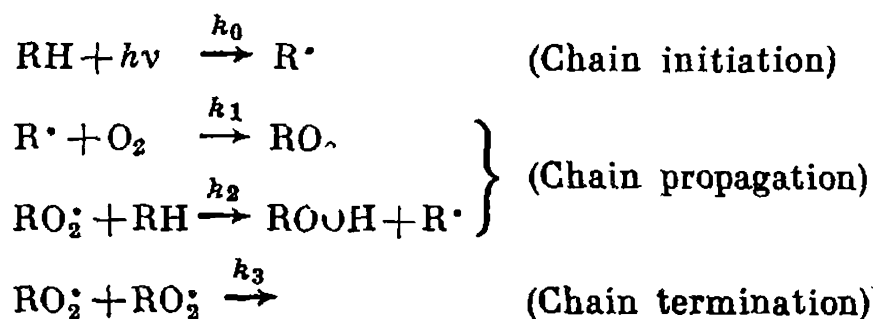
Since the chain terminates at the Cl atom, it may be assumed that $k_i = k_1$, $[A_i] = [\text{HCOOH}]$. Since $w_0 = k_0 [\text{Cl}_2]$, then

$$w = \frac{k_0 k_1}{k_3} [\text{Cl}_2] [\text{HCOOH}]$$

Hence,

$$k = k_0 k_1 / k_3$$

4. The photochemical oxidation of 5*M* dibenzyl ether $(\text{CH}_5\text{CH}_2)_2\text{O}$ with molecular oxygen in the liquid phase proceeds as follows:



The activation energy of the reaction is $E = 28.5$ kJ, the luminous flux intensity is $10^{-7} E$ litre $^{-1}$ s $^{-1}$, and the reaction rate is $w = 9.5 \times 10^{-6}$ mole litre $^{-1}$ s $^{-1}$. The chain initiation rate measured by the inhibitor method is $w_0 = 9 \times 10^{-8}$ mole litre $^{-1}$ s $^{-1}$. The activation energy of oxidation of dibenzyl ether in the case of initiation with azo-*iso*-butyronitrile is $E = 93.6$ kJ, and that of its dissociation is $E = 128.9$ kJ. Calculate the chain length and the activation energy of each step.

Solution. The kinetics of the unbranched chain reaction is given by the equation

$$w = k_i \sqrt{w_0/2k_3} [A_i]$$

Since $[A_i] = [\text{RH}]$ and $k_i = k_2$, then $w = \frac{k_2}{\sqrt{2k_3}} \sqrt{w_0} [\text{RH}]$. Consequently,

$$\frac{k_2}{\sqrt{k_3}} = \frac{\sqrt{2} \times 9.5 \times 10^{-6}}{\sqrt{9 \times 10^{-8} \times 5}} = 8.9 \times 10^{-3} \text{ mole}^{-1/2} \text{ litre}^{1/2} \text{ s}^{-1/2}$$

The reaction chain length will be $\nu = w/w_0 = 105$. The activation energy is $E = 0.5E_0 + E_2 - 0.5E_3$. Since photochemical initiation is an elementary photochemical reaction, its activation energy is zero. Hence,

$$E_2 - \frac{1}{2} E_3 = 28.5 \text{ kJ}$$

Since

$$E_2 - 0.5E_3 = E - 0.5E_0 = 93.6 - 0.5 \times 128.9 = 28.9 \text{ kJ}$$

Insofar as the activation energy of the processes of recombination and disproportionation of free radicals approaches zero, $E_2 - 0.5E_3 \approx E_2$.

5. A cylindrical quartz vessel 4 cm in diameter is filled with a stoichiometric mixture $2\text{H}_2 + \text{O}_2$ under a pressure of 10 mm Hg and at 788 K, and a chain reaction takes place in it. Calculate the rate constant of degradation of the H atoms if the efficiency of their capture by quartz is $\mathcal{E}_\text{H} = 1.3 \times 10^{-3}$. The diameter of H atoms is $\sigma_\text{H} = 1.90 \times 10^{-8}$ cm, that of H_2 molecules is $\sigma_{\text{H}_2} = 2.40 \times 10^{-8}$ cm, and that of O_2 molecules, $\sigma_{\text{O}_2} = 2.98 \times 10^{-8}$ cm.

Solution. For a cylindrical vessel, the chain termination rate constant is

$$k_t = \frac{1}{(r^2/8D) + (2r/\mathcal{E}\bar{u})}$$

where r is the radius of the vessel, D is the diffusion coefficient, and \bar{u} is the relative velocity of the atoms.

To calculate the diffusion coefficient use the following formula from the molecular-kinetic theory of gases:

$$D = 1/3 \bar{u} \lambda$$

in which \bar{u} is the velocity of the particles, and λ is the free path length:

$$\lambda = \bar{u} / \sum_i \sigma_i \bar{u}_i n_i$$

where σ_i is the cross section of collisions of the free radical with the i th particle out of all particles present in the reaction vessel, n_i is the number of i particles per cm^3 , and \bar{u} is the relative velocity of the free radicals and i particles. For this system,

$$D = \frac{1}{3} \frac{\bar{u}^2}{\sigma_1 \bar{u}_1 n_1 + \sigma_2 \bar{u}_2 n_2}$$

The relative velocities of the H and H_2 , H and O_2 are

$$\bar{u}_1 = \sqrt{\frac{8RT}{\pi M^*}} = \sqrt{\frac{8 \times 8.31 \times 10^7 \times 788}{3.14 \times 0.66}} = 5.05 \times 10^5 \text{ cm/s}$$

$$\bar{u}_2 = \sqrt{\frac{8 \times 8.31 \times 10^7 \times 788}{3.14 \times 0.97}} = 4.2 \times 10^5 \text{ cm/s}$$

The number of H_2 and O_2 molecules per cm^3 will be

$$n_1 = P \frac{2}{3} \frac{0.97 \times 10^{19}}{T} = 8.2 \times 10^{15} P$$

$$n_2 = P \frac{1}{3} \frac{0.97 \times 10^{19}}{T} = 4.1 \times 10^{15} P$$

The relative velocity of one molecule is

$$\bar{u} = \sqrt{\frac{8 \times 8.31 \times 10^7 \times 788}{3.14}} = 4.15 \times 10^5 \text{ cm/s}$$

The cross sections of collisions of H with H_2 and O_2 are

$$\pi \left(\frac{\sigma_{\text{H}} + \sigma_{\text{H}_2}}{2} \right)^2 = \pi (0.95 + 1.20)^2 \times 10^{-16} = 1.45 \times 10^{-15} \text{ cm}^2$$

$$\pi \left(\frac{\sigma_{\text{H}} + \sigma_{\text{O}_2}}{2} \right)^2 = \pi (0.95 + 1.49)^2 \times 10^{-16} = 1.89 \times 10^{-15} \text{ cm}^2$$

Hence,

$$\begin{aligned} D &= \frac{1}{3} \frac{(4.15 \times 10^5)^2}{1.45 \times 10^{-15} \times 5.05 \times 10^5 \times 8.2 \times 10^{15} P} \\ &\quad + \frac{1.89 \times 10^{-15} \times 4.1 \times 10^{15} \times 4.2 \times 10^5 P}{1.45 \times 10^{-15} \times 5.05 \times 10^5 \times 8.2 \times 10^{15} P} \\ &= \frac{1}{3} \frac{17.22 \times 10^5}{60 \times P + 61.51 \times P} = \frac{6.2 \times 10^3}{P} \text{ cm}^2/\text{s} \end{aligned}$$

Then,

$$\frac{r^2}{8D} = \frac{4^2 \times P}{8 \times 6.2 \times 10^3} = 8 \times 10^{-5} \times P \text{ s} = 8 \times 10^{-4} \text{ s}$$

and

$$\frac{2r}{\xi_u} = \frac{1}{1.3 \times 10^{-3} \times 4.15 \times 10^5} = 7.4 \times 10^{-3} \text{ s}$$

Consequently,

$$k_t = \frac{1}{8 \times 10^{-4} + 7.4 \times 10^{-3}} = \frac{1}{8.2 \times 10^{-3} \text{ s}} = 122 \text{ s}^{-1}$$

Problems

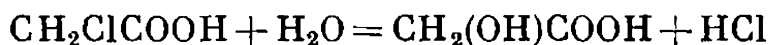
1. A quartz reactor containing benzene saturated with 10% chlorine was exposed to a luminous flux ($\lambda = 313 \text{ nm}$). The exposure time was 35 min. The reaction has yielded hexachlorocyclohexane. Determine the quantum efficiency of the reaction if the energy passing through the quartz reactor containing pure benzene is 46.81 J and that passing through the reactor during the reaction is 4.25 J. The yield of $\text{C}_6\text{H}_6\text{Cl}_6$ was 1.8 g.

2. When a luminous flux at $\lambda = 400 \text{ nm}$ was passed through a reactor in which the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ took place, 100 g of phosgene were produced; the amount of the electromagnetic energy absorbed by the gas was $E_{\text{abs}} = 3 \times 10^2 \text{ J}$. Calculate the quantum efficiency.

3. For a reaction yielding 1 mole of ozone with a quantum efficiency $\gamma = 3$, determine the amount of the electromagnetic energy at $\lambda = 207 \text{ nm}$ to be absorbed by oxygen as it converts into ozone: $3\text{O}_2 = 2\text{O}_3$.

4. Thermal decomposition of acetone at 578 K is 25% complete within 90.9 s, and at 601 K it is 25% complete within 31 s. Its photochemical decomposition takes place at a wavelength of 313 nm with a quantum efficiency $\gamma = 2$. Calculate the rate constant of the monomolecular thermal decomposition of acetone, the activation energy of this process, and the expenditure of electromagnetic energy (J/mole) in the photochemical process. Will the total electromagnetic energy expenditure correspond to the calculated value?

5. Calculate the activation energy for the reaction



if $k_{353 \text{ K}} = 2.22 \times 10^{-5} \text{ min}^{-1}$ and $k_{403 \text{ K}} = 2.37 \times 10^{-3} \text{ min}^{-1}$ and compare it with the energy received by the system during photochemical activation by illumination at a wavelength of 253.7 nm with a quantum efficiency $\gamma = 1$. How will the valence of chlorine change

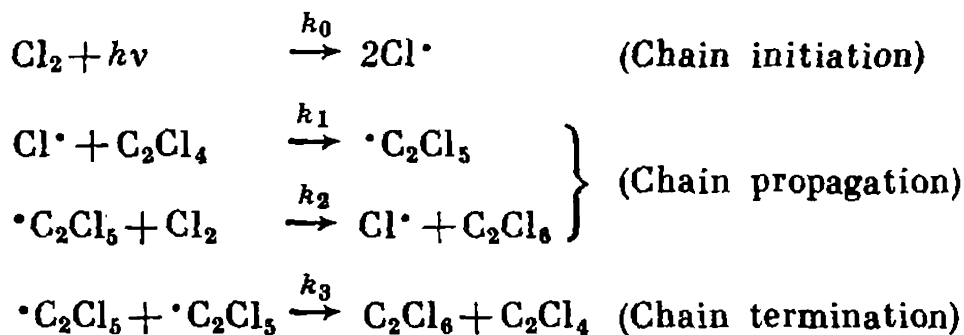
in this reaction? How and why will the electrolytic conductance change in the course of time?

6. Derive a system of equations for chain initiation and propagation in the gaseous mixture $\text{H}_2 + \text{Cl}_2$ during the photochemical reaction. Will a luminous flux at $\lambda = 475.8 \text{ nm}$ be sufficient for chain initiation? What are the heats of the elementary steps? Calculate the amount of absorbed luminous energy during formation of 1 mole HCl with a quantum efficiency $\gamma = 10^5$. Mark the free radicals with dots.

7. The kinetics of photochemical chlorination of tetrachloroethylene in a CCl_4 solution is given by the equation

$$\frac{d[\text{C}_2\text{Cl}_6]}{dt} = k[\text{Cl}_2]^{3/2}$$

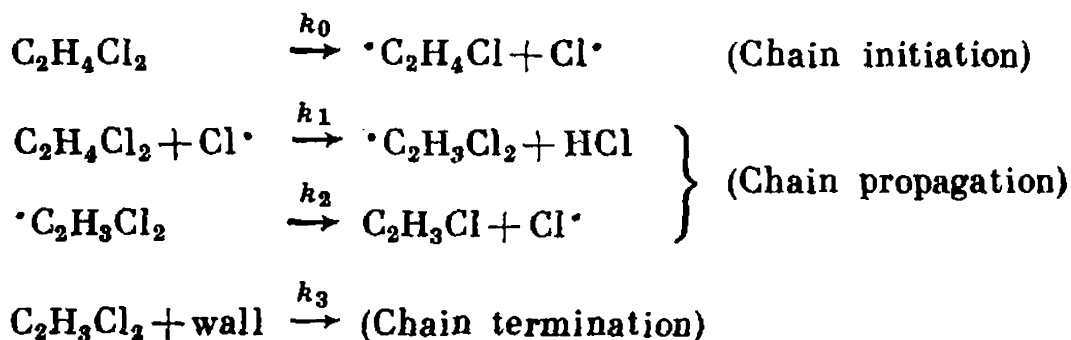
The high quantum efficiency indicates that this is a chain reaction, which is also indicated by the fractional order of the reaction. Derive the reduced differential equation if the reaction proceeds as follows:



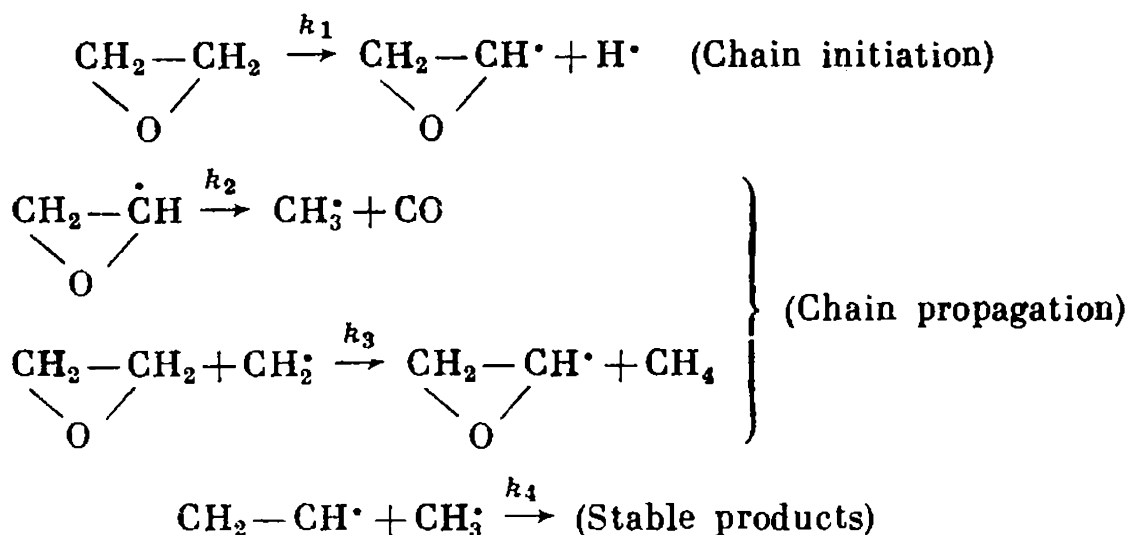
8. The kinetics of thermal decomposition of dichloroethane in the gas phase is given by the first-order equation

$$-\frac{d[\text{C}_2\text{H}_4\text{Cl}_2]}{dt} = k[\text{C}_2\text{H}_4\text{Cl}_2]$$

Derive the reduced differential equation if the reaction proceeds as follows:

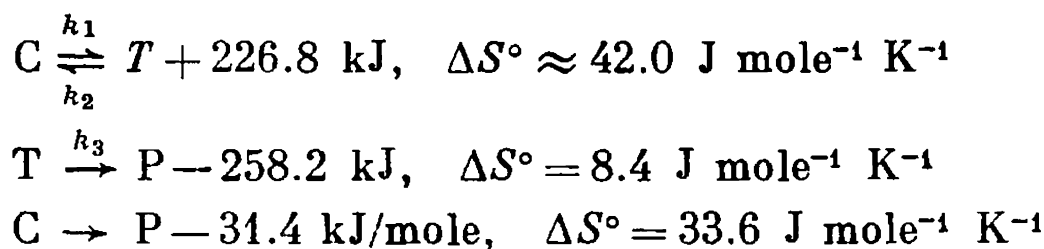


9. The following mechanism has been proposed for thermal decomposition of ethylene oxide:



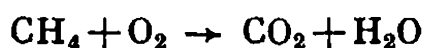
Assuming that the radical concentrations are steady, prove that the decomposition reaction is of the first order with respect to ethylene oxide.

10. At 300 K, the dissociation of cyclopropane (C) yielding propylene (P) involves intermediate formation of the trimethylene biradical (T).

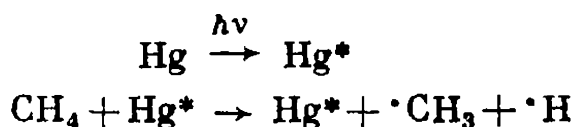


Express the isomerization rate in terms of the constants k_1 , k_2 , and k_3 (ignore pressure variations). Calculate the total activation energy of isomerization if the activation energy for k_3 is 46.2 kJ/mole and $E_2 = 16.8$ kJ/mole. Calculate the mean lifetime of the particle T in the system if $k_{02} = 1 \times 10^{14} \text{ s}^{-1}$. Determine the rate constant for the overall decomposition process if the pre-exponential factor is $k_{03} = 2 \times 10^{13} \text{ s}^{-1}$.

11. The reaction of CH_4 oxidation with oxygen



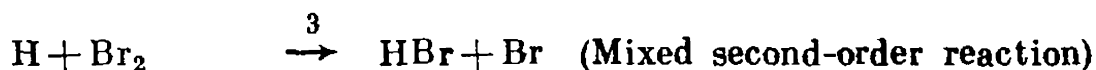
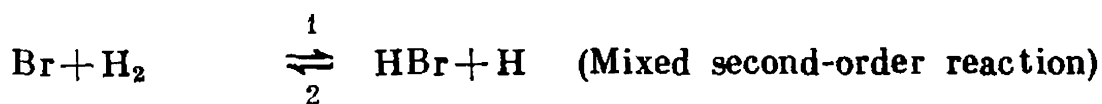
was conducted with photosensitization:



The $\cdot\text{CH}_3$ radicals react with O_2 yielding a mixture of products CO_2 , CO , and $\text{HC}\begin{array}{c} \diagup \text{O} \\ \diagdown \text{H} \end{array}$. The main reaction product is carbon dioxide,

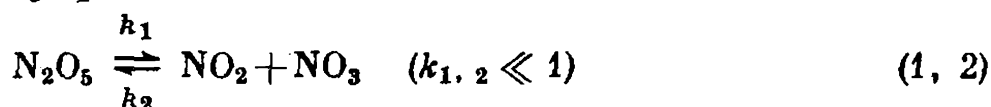
CO_2 . The amount of reacted CH_4 was 6.1×10^4 molecules/s. The electromagnetic energy was 8.7×10^{-14} J/s, the experimental temperature was 298 K, and $\lambda = 253.7$ nm. Determine the quantum efficiency of the reaction.

12. The photosensitized reaction between bromide and hydrogen with excess H_2 at 423 K is a chain process and proceeds as follows:



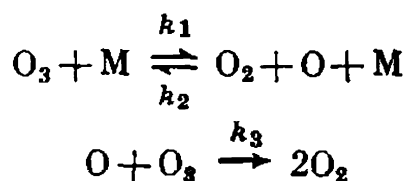
Using the steady concentration method, express the steady concentrations of the H and Br atoms in terms of concentrations of the other products, rate constants, and the initiation reaction rate. Write the differential equation for the steady HBr formation rate. Calculate the quantum efficiency of HBr formation. Under what conditions will the quantum efficiency be maximum? What is the physics behind this phenomenon?

13. The chain reaction of O_2 dissociation in the gas phase, which is catalyzed by N_2O_5 , proceeds as follows:



Assuming that reaction (1) is of the first order, while the rest of the reactions are of the second order, write the equations for the rates at which the initial substances are spent and the end and intermediate products accumulate. Use the steady concentration method to calculate the steady concentrations of NO_2 and NO_3 . Express the O_3 spending rate in terms of O_3 and N_2O_5 concentrations (N_2O_5 is not spent in the reaction). Write the equation for the O_3 spending rate if the reaction $\text{O}_3 + \text{NO} \xrightarrow{k_5} 2\text{O}_2 + \text{NO}_2$ is substituted into the above scheme for reaction (4). Is it possible to establish experimentally the difference between the derived rate equations?

14. The reaction of thermal decomposition of ozone proceeds as follows:

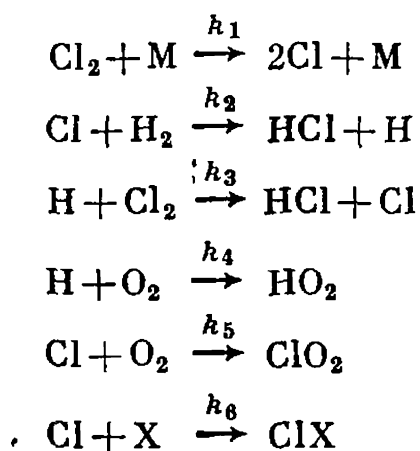


where M is a valence-saturated molecule. Using the steady concentration method, derive the equation for the ozone decomposition rate:

$$-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_3[\text{O}_3]^2[\text{M}]}{k_2[\text{O}_2][\text{M}] + k_3[\text{O}_3]}$$

Use this equation and the activation energies $E_1 = 103.0$ kJ/mole, $E_2 = 0$ kJ/mole, and $E_3 = 12.6$ kJ/mole to calculate the effective activation energy for the ozone decomposition reaction (a) in a complete absence of oxygen and (b) with excess oxygen.

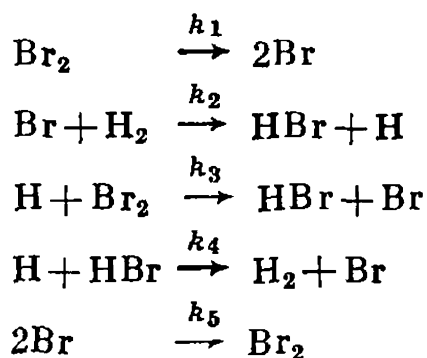
15. Use the steady concentration method to derive the expression for the rate of the reaction between chlorine and hydrogen, proceeding as follows:



where M is a substance (which may be the reaction vessel surface as well) that affects the dissociation of chlorine molecules, and X is a substance that binds the chlorine atoms. The rate of hydrogen chloride formation may be assumed equal to $k_3[\text{H}][\text{Cl}_2]$. Since $k_2 \ll k_3$, the terms with $[\text{H}][\text{O}_2]^2$ can be ignored.

Derive the expression for the reaction rate (a) in complete absence of oxygen and (b) in the presence of oxygen. Proceeding from the following values: $E_1 = 117.4$ kJ/mole, $E_2 = 25.2$ kJ/mole, $E_3 = 8.4$ kJ/mole, $E_4 = 0$ kJ/mole, and $E_5 = 0$ kJ/mole, calculate the effective activation energy for both cases.

16. The mechanism of the reaction $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$ is



The chain carriers are the hydrogen and bromine atoms. The hydrogen bromide formation rate is given by the equation

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

Some transformations and substitutions give the following equation:

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[\text{H}_2][\text{Br}_2]^{1/2}}{1 + (k_4/k_3)/([\text{HBr}]/[\text{Br}_2])}$$

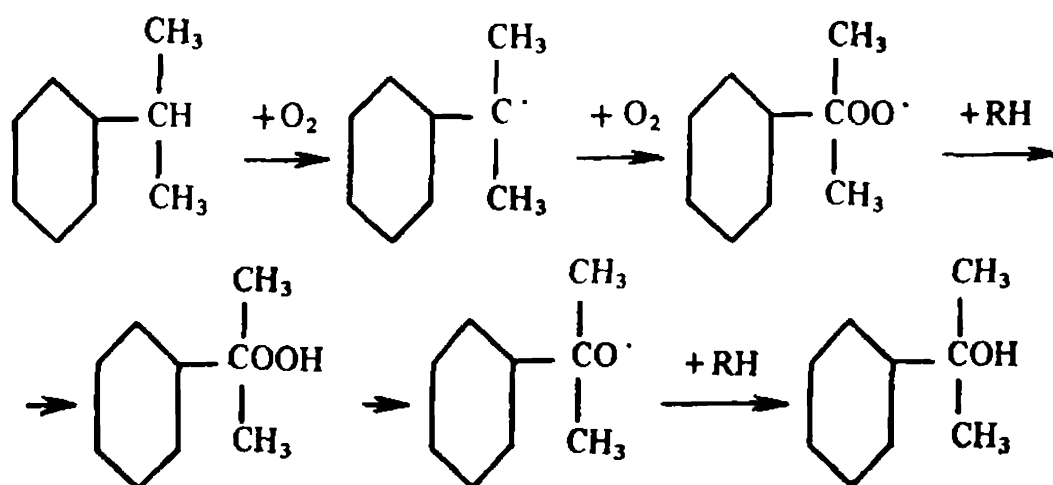
Use this equation and the following values of the activation energy: $E_1 = 189.5$ kJ/mole, $E_2 = 740$ kJ/mole, $E_3 = 5.04$ kJ/mole, $E_4 = 5.04$ kJ/mole, and $E_5 = 0$ kJ/mole, calculate the effective activation energy of the reaction between bromine and hydrogen (a) at the onset of the process and (b) with high excess of hydrogen bromide.

17. Calculate the activation energy for the chain initiation reaction involved in oxidation of butane if the reaction parameters 100 s after its onset are as follows:

T , K	540	543	553
φ , s ⁻¹	2.5×10^{-2}	2.3×10^{-2}	2.0×10^{-2}
n , cm ³ s ⁻¹	2.16×10^9	1.98×10^9	1.86×10^9

The oxidation of butane is a branched chain reaction.

18. Experiments with the chain reaction of isopropyl benzene oxidation:



have yielded the following results:

t , h	w , mole litre ⁻¹ h ⁻¹	w_0 , mole litre ⁻¹ h ⁻¹	$\frac{w}{\sqrt{[\text{ROOH}]}}$	$[\text{RH}]$, mole/litre
1.00	0.20	0.106	0.630	10
2.00	0.417	—	—	—
2.83	0.556	—	—	—
3.67	0.750	—	—	—

Determine the chain length and write the expression for the chain branching rate.

19. Figure 48 shows the inflammability limits for the $\text{CO} + \text{O}_2$ system. Describe the relationship between these limits and temper-

ature as well as the composition of the gaseous mixture and explain the low and upper inflammability limits. What radicals can lower the ignition temperature in the presence of moisture in this gaseous mixture?

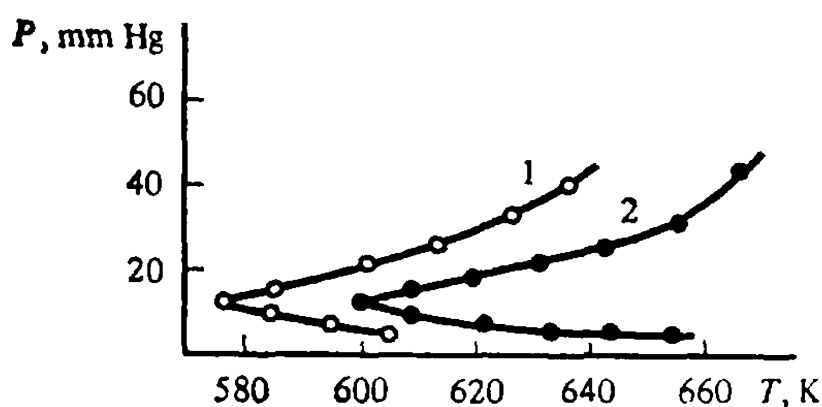


Fig. 48. Inflammability limits at different O_2 contents:
1—90% O_2 ; 2—33% O_2

20. A spherical quartz vessel 10 cm in diameter is filled with the stoichiometric mixture $2H_2 + O_2$ under a pressure of 20 mm Hg and at 515 K, and a chain reaction takes place in this vessel. Calculate the rate constant of degradation of the H atoms if the efficiency of their capture with quartz is $\xi_H = 1.3 \times 10^{-3}$. The atomic diameters are as follows (cm): H 1.90×10^{-8} , H_2 2.40×10^{-8} , O_2 298×10^{-8} .

21. Determine the energy of the absorbed light in the photochemical reaction $Br_2 + C_6H_{12} \xrightarrow{h\nu} C_6H_{11}Br + HBr$ if one mole of Br_2 reacts during illumination. The monochromatic light wavelength is 470 nm. The quantum efficiency is $\gamma = 1$.

22. Determine the energy of the absorbed light in the photochemical reaction $CH_3COOH \xrightarrow{h\nu} CH_4 + CO_2$ if one mole of acetic acid reacts during illumination. The monochromatic light wavelength is 230 nm. The quantum efficiency is $\gamma = 0.5$.

23. Proceeding from the data of the handbook, determine the energy of the monochromatic light absorbed during dissociation of one mole of CH_3COCH_3 in the reaction $CH_3COCH_3 \xrightarrow{h\nu} C_2H_6 + CO$ proceeding in the gas phase at 333 K.

Multivariant Problem

The reaction $A_1 + A_2 = B_1 + B_2$ is an unbranched chain reaction. The chain initiation results from interaction between a light quantum and one of the reactants or from heating. Assuming that the chain propagation reaction involves two elementary steps and that the chain termination occurs at one of the free radicals participating in the process, (1) write the scheme of the expected chain reaction mechanism, (2) derive the stoichiometric equation of the chain reac-

tion, based on the chain length ν , (3) derive the kinetic equation for the reaction under consideration, proceeding from the proposed mechanism and prove that, depending on the nature of the free radical at which the chain terminates, the reaction can be described by different kinetic equations, and (4) determine the number of A_1 molecules spent and that of B_1 molecules formed in the chain if the chain length is ν .

Variant	Reaction	Reactant interacting with a light quantum or undergoing thermal decomposition	Chain length ν	Free radical at which the chain terminates	Dissociating molecule	Emerging molecule	T, K
1	$\text{Cl}_2 + \text{HCOOH} \xrightarrow{h\nu} \text{HCl} + \text{CO}_2$	Cl_2	30	$\text{Cl}\cdot$	HCOOH	HCl	298
2	$\text{C}_2\text{H}_6 + 6\text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6 + 6\text{HCl}$	Cl_2	45	$\cdot\text{C}_2\text{H}_5$	Cl_2	C_2Cl_6	298
3	Thermal decomposition of $\text{C}_2\text{H}_4\text{Cl}_2$	$\text{C}_2\text{H}_4\text{Cl}_2$	50	$\cdot\text{C}_2\text{H}_3\text{Cl}_2$ $\cdot\text{C}_2\text{H}_3\text{Cl}_2$	$\text{C}_2\text{H}_4\text{Cl}_2$ $\text{C}_2\text{H}_4\text{Cl}_2$	HCl HCl	298 300
4	$\text{Cl}_2 + \text{H}_2 \xrightarrow{h\nu} 2\text{HCl}$	Cl_2	35	$\text{Cl}\cdot$	Cl_2	HCl	300
5	$\text{Cl}_2 + \text{H}_2 \xrightarrow{h\nu} 2\text{HCl}$	Cl_2	45	$\text{H}\cdot$	H_2	HCl	300
6	$\text{Br}_2 + \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{h\nu} \text{C}_6\text{H}_5\text{CH}_2 - \text{CH}_2\text{C}_6\text{H}_5 + \text{HBr} + \text{C}_6\text{H}_5\text{CH}_2\text{Br}$	Br_2	20	$\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$	$\text{C}_6\text{H}_5\text{CH}_3$	HBr	300
7	$\text{CO} + \text{Cl}_2 \xrightarrow{h\nu} \text{COCl}_2$	Cl_2	500	$\dot{\text{Cl}}$	Cl_2	COCl_2	300
8	$\text{CO} + \text{Cl}_2 \xrightarrow{h\nu} \text{COCl}_2$	Cl_2	300	$\dot{\text{Cl}}$	CO	COCl_2	300
9	Pyrolysis of methane	CH_4	100	$\text{H}\cdot$	CH_4	C_2H_6	1000
10	Pyrolysis of methane	CH_4	80	$\text{H}\cdot$ CH_3	CH_4	H_2	1000
11	$\text{H}_2 + \text{Br}_2 \xrightarrow{h\nu} 2\text{HBr}$	Br_2	70	$\dot{\text{Br}}$	Br_2	HBr	300
12	$\text{H}_2 + \text{Br}_2 \xrightarrow{h\nu} 2\text{HBr}$	Br_2	50	$\cdot\text{H}$	H_2	HBr	300
13	$2\text{O}_3 \xrightarrow{h\nu} 3\text{O}_2$	O_3	10	$\text{O}\cdot$	O_3	O_2	87
14	Thermal decomposition $\text{CH}_2\text{COCH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{COCH}_3$	CH_2COCH_3	30	$\dot{\text{C}}\text{H}_2\text{COCH}_3$	CH_3COCH_3	CH_4	500
15	Thermal decomposition $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3 + \text{CO} + \text{H}_2$	CH_3OCH_3	50	$\dot{\text{C}}\text{H}_3$	CH_3OCH_3	CH_4	500

CHAPTER 26

Diffusion.

Kinetics of Heterogeneous Processes

Basic Equations and Symbols

The diffusion process is given by Fick's equations. The differential form of the first equation is

$$\frac{dn}{dt} = -D \frac{dc}{dx} S \quad (26.1)$$

and that of the second equation is

$$\left(\frac{\partial c}{\partial t} \right)_x = D \left(\frac{\partial^2 c}{\partial x^2} \right)_t \quad (26.2)$$

where dn stands for the amount of a substance passing through the surface having area S within time dt , in moles, $\frac{dc}{dx}$ (grad c) being the concentration gradient. The latter depends on the concentration $\left[\frac{dc}{dx} = f(c) \right]$. In a steady flow,

$$\frac{dc}{dx} = \text{const} = \frac{c_1 - c_2}{\Delta x}$$

$\left(\frac{\partial c}{\partial t} \right)_x$ is the change in the concentration of the substance undergoing diffusion at a given point in the system, in the course of time; D is the diffusion coefficient;

$$D = D_0 e^{-E_0/RT} \quad (26.3)$$

where D_0 is a constant, and E_0 is the activation energy of the diffusion process. The integral forms of Fick's equations are as follows: the first equation for steady flow

$$J_{i(x)} = \frac{n}{t} = -D \frac{\Delta c}{\Delta x} S \quad (26.4)$$

the second equation (for nonsteady flow if the diffusion occurs in a body of infinite extent, which means that x varies from $-\infty$ to $+\infty$) has the solution

$$c = \frac{c_0}{2} (1 - \text{erf } Z) \quad (26.5)$$

Then

$$J_{i(x=0)} = \frac{c_0}{\sqrt{\pi}} \sqrt{\frac{D}{t}} = \frac{n}{t} \quad (26.6)$$

If diffusion takes place in a semi-infinite (semi-bounded) body (with x varying from 0 to $+\infty$), the solution takes the form

$$c = c_s (1 - \operatorname{erf} Z) \quad (26.7)$$

$$J_{i(x=0)} = \frac{2c_s}{\sqrt{\pi}} \sqrt{\frac{D}{t}} = \frac{n}{t} \quad (26.8)$$

where $\operatorname{erf} Z$ is the Gaussian error function. The value of $\operatorname{erf} Z$ is given in reference books as a function of Z :

$$Z = \frac{x}{2\sqrt{Dt}} \quad (26.9)$$

Some limiting values of Z and the corresponding values of $\operatorname{erf} Z$ are given below:

$$\begin{array}{ccccc} Z & 0 & \geq 2.8 & \leq 0.7 & \\ \operatorname{erf} Z & 0 & 1 & Z & \end{array}$$

Equations (26.5) through (26.8) are applicable provided

$$l \geq 5.6 \sqrt{Dt} \quad (26.10)$$

where $l = x_{\max}$ is the thickness of the substance layer in which the diffusion occurs;

$$5.6 \sqrt{Dt} = L \quad (26.10a)$$

where L is the distance covered by the diffusion front within time interval t .

The diffusion coefficient can be expressed as the friction coefficient in the Stokes-Einstein equation

$$D = \frac{RT}{N_A 6\pi\eta r} \quad (26.11)$$

in which η is the viscosity coefficient, and r is the radius of the spherical particles involved in the diffusion.

The rate of dissolution with constant agitation is given by Fick's equation whose differential form is

$$\frac{dn}{dt} = \frac{DS}{V\delta} (c_s - c) \quad (26.12)$$

where D is the diffusion coefficient of the solute, S is the area of the solute surface, V is the solvent volume, δ is the thickness of the surface layer, c_s is the concentration of the saturated solution, in mole/litre, and c is the solution concentration.

$$DS/V\delta = k_{\text{dissol}} \quad (26.13)$$

If $c = \text{const}$, dissolution becomes a steady-state process, $(c_s - c)/\delta = \text{const}$, and the integral form of Eq. (26.12) is

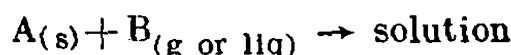
$$\Delta n = DS/V\delta (c_s - c) t \quad (26.14)$$

where Δn is the amount of the substance dissolved within time interval t .

If the concentration c changes during dissolution, then

$$k_{\text{dissol}} = \frac{2.3}{t_2 - t_1} \log \frac{c_s - c_1}{c_s - c_2} \quad (26.15)$$

The effective rate constant for a heterogeneous monomolecular reaction



(the agitation rate being constant) is

$$k^* = \beta k / (k + \beta) \quad (26.16)$$

where k is the rate constant of the first-order chemical reaction proper, and β is the diffusion rate constant (the rate at which the substance is transferred into the reaction zone per unit surface area

$$\beta = D/\delta \quad (26.17)$$

δ being the distance covered by the transferred reactant.

For a reaction proceeding in the diffusion region ($k^* = \beta$), the kinetic equations take the following form: differential form

$$-\frac{dn}{dt} = \beta S (c - c_0) \quad (26.18)$$

in which c and c_0 stand for the concentrations of reactant B within the solution and near the surface of reactant A, respectively. At $c = c_0$,

$$-\frac{dc}{dt} = \beta \frac{S}{V} c \quad (26.19)$$

integral form:

$$k = \frac{2.3}{t_2 - t_1} \log \frac{c_1}{c_2} \quad (26.20)$$

$$k = \frac{D}{\delta} \frac{S}{V} \quad (26.21)$$

With reactions of the $A_{(s)} + B_{(g)} = AB_{(s)}$ type, when the layer formed by reaction product AB is porous and does not hinder contact between reactants A and B and the reaction proceeds in the kinetic region, the reaction may be of the zeroth, first, second, and fractional order. In the case of zeroth-order reactions, the integral form of the kinetic equation is

$$\frac{\Delta m}{S} = k'' t \quad (26.22)$$

where Δm is the increase in the weight of reactant A as a result of formation of the AB layer on it, S is the reaction surface area ($S = \text{const}$), and k is the rate constant.

If reactant A and B contact through a dense layer of AB, the reaction is, as a rule, limited by diffusion, and the integral form of the kinetic equation is a parabolic equation:

$$\left(\frac{\Delta m}{S}\right)^2 = k''t \quad (26.23)$$

where k'' is the rate constant proportional to the coefficient D of diffusion of reactant A or B through the layer of end product AB.

The evaporation rate is given by the equation

$$J_{\text{evap}} = \frac{P_s}{\sqrt{2\pi MRT}} \quad (26.24)$$

where J_{evap} is the number of moles of the liquid, evaporated per unit time from unit surface area (evaporation rate), and P_s is the saturated vapour pressure.

Exercises

1. A specimen of an alloy of metals A and B, 0.5 cm long, has been welded to a specimen of metal B of the same length. Determine the time it will take for a relative concentration of metal A (c_A/c_0) to become equal to 0.2 inside the pure ingot of metal B, as a result of diffusion from the alloy, at distances of 0.01 and 0.2 cm from the weld, and for the diffusion coefficient ($D = \text{const}$) to become equal to $2 \times 10^{-9} \text{ cm}^2/\text{s}$.

Solution. To determine the diffusion time use Fick's equations (26.5) and (26.9). First, calculate t for $x = 0.01 \text{ cm}$ after having determined Z from the equation

$$c/c_0 = \frac{1}{2} (1 - \text{erf } Z), \quad 0.2 = \frac{1}{2} (1 - \text{erf } Z), \quad \text{erf } Z = 0.6 \simeq Z$$

Then, calculate t using the equation

$$Z = \frac{x}{2\sqrt{\Delta t}}, \quad \sqrt{t} = \frac{x}{Z2\sqrt{D}} = \frac{0.01}{0.6 \times 2\sqrt{2 \times 10^{-9}}}, \quad t = 9.6 \text{ h}$$

Check the validity of the results and applicability of Eq. (26.5). To this end, substitute the found values into Eq. (26.10):

$$0.5 \geq 5.6 \sqrt{2 \times 10^{-9} \times 9.6 \times 3600} \geq 0.046$$

The conditions under which Eq. (26.5) is applicable are met:

$$l(x_{\text{max}}) > 5.6 \sqrt{Dt}$$

Repeat the calculation and determine t for $x = 0.2 \text{ cm}$:

$$Z = 0.6 = \frac{0.2}{2\sqrt{2 \times 10^{-9} t}}, \quad t = 3875 \text{ h}$$

Check whether Eq. (26.5) is applicable for $x = 0.2$ cm:

$$0.5 \geq 5.6 \sqrt{2 \times 10^{-9} \times 3875 \times 3600} \geq 0.93$$

The applicability condition is not met: $l(x_{\max}) < 5.6 \sqrt{Dt}$. The last result is not valid.

2. Calculate the time it will take for the width of the diffuse zone between alloy AB and metal B to become equal to 0.1 cm and $D = \text{const} = 2 \times 10^{-9}$ cm/s.

Solution. The width δ of the diffuse zone in the case of diffusion in an infinitely long body (implying the distance between the diffusion fronts) is $2L$ or

$$\delta = 2L = 2 \times 5.6 \sqrt{Dt}, \quad 2.56 \sqrt{2 \times 10^{-9} t} = 0.1, \quad t = 11 \text{ h}$$

3. A sugar layer has been placed on the bottom of a cylindrical vessel filled with water. As the sugar dissolves, it diffuses into the solution. The solution above the sugar is saturated, and its concentration c_s is constant. The height of the water column is 20 cm. Calculate the distance x from the sugar-solution interface, at which the relative concentration c/c_s becomes equal to 0.8 after 16 days; $D = 0.25$ cm²/day. Remember that, according to Eq. (26.10), for the above conditions (t, D) $l = 11.2$ cm at 298 K.

Solution. Since we are dealing with nonsteady diffusion in a semi-infinite space, use Eqs. (26.7) and (26.9) for the calculation:

$$0.8 = (1 - \text{erf } Z), \quad \text{erf } Z = 0.2, \quad Z = 0.2$$

$$0.2 = x/2 \sqrt{0.25 \times 16}, \quad x = 0.8 \text{ cm}$$

Equation (26.7) is applicable to the above conditions because $l > x$ ($11.2 > 0.8$).

4. A sugar layer has been placed on the bottom of a cylindrical vessel filled with water. As the sugar dissolves, it diffuses into the solution. The solution above the sugar is saturated and its concentration c_s is constant. The height of the water column is 20 cm, and $D = 0.25$ cm²/day. Calculate the amount of sugar that will pass into the solution from 1 cm² of the surface within 16 days if $c_s = 2.565$ mole/litre.

Solution. Calculate the number of moles of the sugar dissolved within 16 days using Eq. (26.8):

$$J = \frac{2c_s}{\sqrt{\pi}} \sqrt{\frac{D}{t}} = \frac{2 \times 2.565}{1000 \sqrt{\pi}} \sqrt{\frac{0.25}{16}} = 2.61 \times 10^{-4} \text{ mole h}^{-1} \text{ cm}^{-2}$$

$$\Delta n = Jt = 2.61 \times 10^{-4} \times 16 = 5.776 \times 10^{-3} \text{ mole cm}^2$$

$$m_{\text{sugar}} = 5.776 \times 10^{-3} \times 342.3 = 1.977 \text{ g/cm}^2$$

5. Calculate the radius of a protein molecule if the coefficient of its diffusion in a sugar solution is $D = 6.39 \times 10^{-7} \text{ cm}^2/\text{s}$, $T = 298 \text{ K}$. Assume that the protein molecules are spherical.

Solution. To calculate the molecular radius of the protein use the equation

$$r = \frac{RT}{DN_A 6\pi\eta}$$

where $\eta = 1.227 \times 10^{-3} \text{ Pa s}$ (handbook);

$$r = \frac{(8.314 \text{ J mole}^{-1} \text{ K}^{-1}) (298 \text{ K})}{(6.39 \times 10^{-11} \text{ m}^2/\text{s}) (6.02 \times 10^{23} \text{ mole}^{-1}) 6 \times 3.14 (1.227 \times 10^{-3} \text{ Pa s})} = 2.79 \times 10^{-9} \text{ m}$$

6. A benzoic acid pellet surface area $S = 2 \text{ cm}^2$ has been placed in a benzoic acid solution. The solution volume was 20 litres and the concentration was 0.003 mole/litre. The solution was stirred so that 0.001 mole $\text{C}_6\text{H}_5\text{COOH}$ was dissolved within 5 min. It may be assumed that the solution concentration remained virtually the same. The acid concentration in the saturated solution was $c_s = 0.024 \text{ mole/litre}$ (298 K). The benzoic acid diffusion coefficient was $D = 0.75 \text{ cm}^2/\text{day}$. Calculate the dissolution rate constant k , the diffusion rate β , and the surface layer thickness δ .

Solution. The concentration at the surface layer-pellet interface is constant and equal to c_s . The concentration in the solution within the same period of time is also constant, therefore, the flow of the substance through the surface layer may be considered steady and

$$\frac{dc}{dx} = \frac{\Delta c}{\Delta x} = \frac{c_s - c}{\delta}$$

For a steady flow Eq. (26.12) takes the form

$$\frac{dn}{dt} = \frac{\Delta n}{t} = \frac{DS}{\delta} (c_s - c)$$

Use Eq. (26.13) to calculate the rate constants after having found DS/δ :

$$\frac{DS}{\delta} = \frac{\Delta n}{t(c_s - c)} = \frac{0.001 \times 60 \times 24}{5(0.024 - 0.003)} = 13\,714 \text{ cm}^3/\text{day}$$

Substitute the numbers into Eq. (26.13):

$$k = \frac{13\,714}{20 \times 10^3} = 0.6857 \text{ day}^{-1}, \quad \beta = \frac{D}{\delta} = \frac{13\,714}{2} = 6857 \text{ cm/day}$$

$$\delta = \frac{DS}{13\,714} = \frac{0.75 \times 2}{13\,714} = 1.09 \times 10^{-4} \text{ cm}$$

7. The concentration of an acid in a saturated solution is $c_s = 0.024 \text{ mole/litre}$ (298 K). The coefficient D for $\text{C}_6\text{H}_5\text{COOH}$ is $0.75 \text{ cm}^2/\text{day}$. The solution concentration varies in the course of

dissolution. A benzoic acid pellet with surface area $S = 2 \text{ cm}^2$ is placed in the benzoic acid solution. The volume of the solution is 20 litres, and its concentration is 0.003 mole/litre. The solution is stirred, and 0.001 mole $\text{C}_6\text{H}_5\text{COOH}$ is dissolved within 5 min. Determine the time it will take for the solution concentration to reach 0.012 mole/litre.

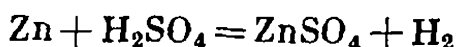
Solution. Since the solution concentration varies within the time period under consideration, the concentration gradient in the surface layer also varies, that is diffusion process is not steady. Use Eq.(26.15). Since $t_1 = 0$ and $c_1 = 0$, we have

$$k = \frac{2.3}{t_2} \log \frac{c_s - c_1}{c_s - c_2}$$

Substitute the numbers and solve the equation for t :

$$t_2 = \frac{2.3}{0.6857} \log \frac{0.024 - 0.003}{0.024 - 0.012} = 0.815 \text{ day or } 19.55 \text{ h}$$

8. Metallic zinc with a surface area of 20 cm^2 was dissolved at 298 K in 700 cm^2 of sulphuric acid according to the equation



Calculate the diffusion rate β and the diffusion layer thickness ratio δ_1/δ_3 in experiments 1 and 3, proceeding from the following data:

The agitation speed is 400 rpm

Experiment		1	2
$t, \text{ h}$	0	0.5	1
$c_{\text{H}_2\text{SO}_4}, \text{ g-equiv/litre}$	0.153	0.118	0.090

The agitation speed is 216 rpm

Experiment		3
$t, \text{ h}$	0	0.5
$c_{\text{H}_2\text{SO}_4}, \text{ g-equiv/litre}$	0.080	0.069

Solution. Determine the dissolution rate constant using Eqs. (26.20) and (26.21). At $t = 0$,

$$k = \frac{2.3}{t_2} \log \frac{c_{t=0}}{c_t}$$

Determine the diffusion rate β for experiment 1:

$$k_1 = \frac{2.3}{0.5} \log \frac{0.153}{0.118} = 0.519 \text{ h}^{-1}$$

$$\beta_1 = \frac{Vk}{S} = \frac{700 \times 0.519}{20} = 18.27 \text{ cm/h}$$

Do the same for experiment 3:

$$k_3 = \frac{2.3}{0.5} \log \frac{0.080}{0.069} = 0.296 \text{ h}^{-1}$$

$$\beta_3 = \frac{700 \times 0.295}{20} = 10.32$$

Use the obtained values of β to calculate the diffusion layer thickness:

$$\delta_1 = \frac{D}{\beta_1} \text{ and } \delta_3 = \frac{D}{\beta_3}, \quad \frac{\delta_1}{\delta_3} = \frac{3}{1} = \frac{10.32}{18.27} = 0.56$$

The diffusion layer thickness is reduced almost to one half after changing the agitation speed.

9. Air is passed over carbon at a constant pressure, which leads to the reaction $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$. The measurement results have made

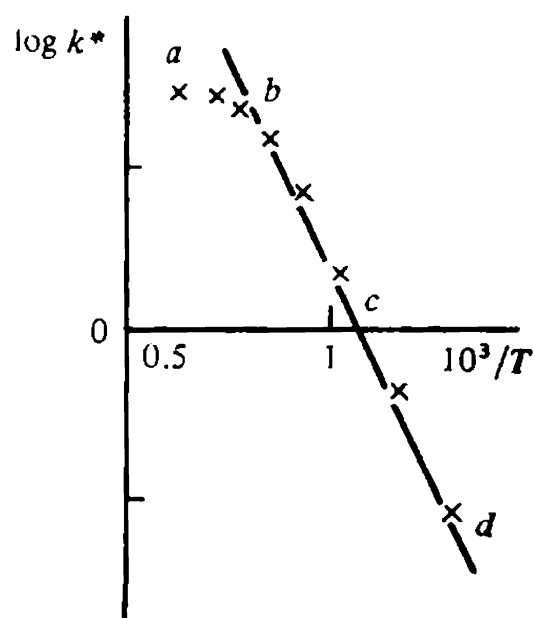


Fig. 49. $\log k$ versus $1/T$ for the reaction of carbon oxidation with atmospheric oxygen

it possible to determine the effective rate constant k^* at different temperatures. The measurement and calculation results are summarized below:

$T, \text{ K}$	777	873	973	1073	1173	1273	1373	1573
$(1/T) \times 10^3$	1.290	1.145	1.026	0.930	0.85	0.785	0.728	0.636
$k^*, \text{ cm/s}$	0.073	0.447	2.15	6.81	13.72	19.49	23.40	26.90
$\log k^*$	-1.137	-0.35	0.332	0.832	1.137	1.29	1.369	1.429

Establish the region in which the reaction occurs and calculate its activation energy.

Solution. Plot $\log k^*$ versus $1/T$ (Fig. 49). Portion dc corresponds to the kinetic region, i.e. the reaction rate is limited by the kinetics proper at $T < 1100 \text{ K}$, $k \ll \beta$; $k = k^*$. At $T > 1100 \text{ K}$, portion cb corresponds to the transition region, i.e. the diffusion rate constants β and the kinetic rate constants k are commensurate. The relationship

between k^* , k , and β is given by Eq. (26.16). Find the activation energy E_{kin} using the equation

$$E_{\text{kin}} = -\tan \alpha \cdot 2.3R$$

where $\tan \alpha$ is determined from the plot of Fig. 49:

$$\tan \alpha = 5.573 \times 10^3$$

Calculate the activation energy:

$$E_a = 5.573 \times 10^3 \times 2.3 \times 8.314 = 106.97 \text{ kJ/mole}$$

10. Air is passed over carbon at a constant pressure, which leads to the reaction $\text{C} + \text{O}_2 = \text{CO}_2$. The effective rate constant k^* was determined at different temperatures. The measurement and calculation results are given below:

$T, \text{ K}$	777	873	973	1073	1173	1273	1373	1573
$(1/T) \times 10^3$	1.290	1.145	1.026	0.930	0.85	0.785	0.728	0.636
$k^*, \text{ cm/s}$	0.073	0.447	2.15	6.81	13.72	19.49	23.40	26.90
$\log k^*$	-1.137	-0.35	0.332	0.832	1.137	1.29	1.369	1.429

Derive an equation of the following type:

$$\log k = A/T + \text{const}$$

Solution. Comparison of the equation $\log k = A/T + \text{const}$ with Eq. (23.4) gives

$$A = -\frac{E}{2.3R} = \frac{-25.47 \times 10}{2.3 \times 1.98} = -5.573 \times 10^3$$

To calculate the constant substitute the values of $\log k$ and $1/T$, related to the kinetic region in which the reaction proceeds at 973 K, into the equation of interest:

$$0.332 = -5.573 \times 10^3/973 + \text{const}$$

hence, $\text{const} = 6.06$. Substitution of the numbers gives

$$\log k = 6.06 - 5573/T$$

11. Air is passed over carbon at a constant pressure, which leads to the reaction $\text{C} + \text{O}_2 = \text{CO}_2$. The effective rate constant k^* was determined at different temperatures:

$T, \text{ K}$	777	873	973	1073	1173	1273	1373	1573
$k^*, \text{ cm/s}$	0.073	0.447	2.45	6.81	1.373	19.49	23.40	26.90

The reaction rate constant is given by the equation

$$\log k = 6.06 - 5573/T$$

Calculate the diffusion rate constant β at 1373 K.

Solution. Calculate the constant β using Eq. (26.16). To this end, use $k^* = 23.40$ cm/s at 1373 K. Calculate the kinetic constant with the aid of the equation

$$\log k = 6.06 - (5573/1373) = 2.00, \quad k = 100 \text{ cm/s}$$

Substitution of the numbers into Eq. (26.16) and calculations give

$$23.40 = \beta \cdot 100 / (100 + \beta), \quad \beta = 30.8 \text{ cm/s}$$

12. Studies into the kinetics of the silver bromination reaction $\text{Ag} + 0.5\text{Br}_2 = \text{AgBr}$ have yielded the following results ($T = 500$ K, $P_{\text{Br}_2} = 170$ mm Hg):

$t, \text{ s}$	1000	2000	3000	4000	6000
$(\Delta m/S) \times 10^2, \text{ g/cm}^2$	1	1.34	1.61	1.84	2.24
$(\Delta m/S)^2 \times 10^4, \text{ g}^2/\text{cm}^4$	1	1.8	2.6	3.4	5

What conclusions can be drawn as regards the reaction type from the experimental results? Calculate the reaction rate constant.

Solution. Since silver bromide forms on metallic silver in the course of the reaction, it may be assumed that the reaction rate will

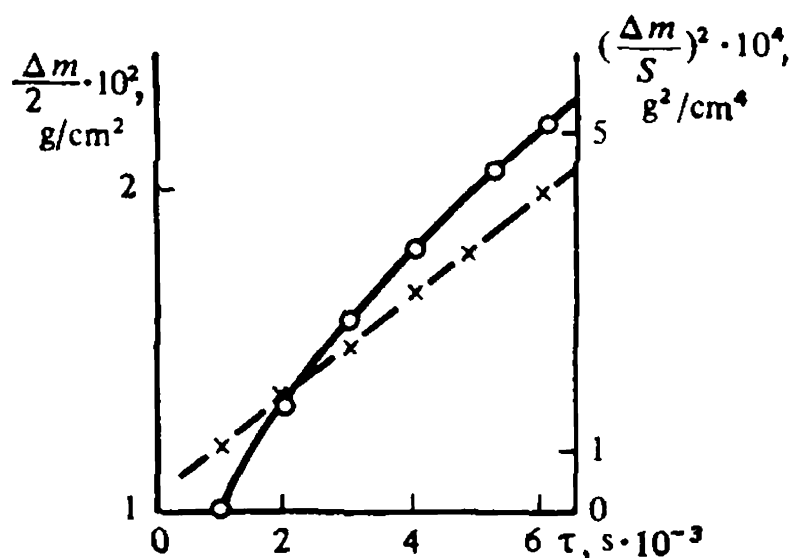


Fig. 50. $\frac{\Delta m}{S}$ and $\left(\frac{\Delta m}{S}\right)^2$ versus t for the thorium oxidation reaction

be limited by that of Ag or Br_2 diffusion through the AgBr layer. To verify this assumption plot the $\Delta m/S = f(t)$ (1) and $(\Delta m/S)^2 = f(t)$ (2) curves. The line drawn in the coordinates $(\Delta m/S)^2$ vs t confirms that the reaction proceeds in the diffusion region. Find the rate constant k^* from the plot as the slope of the straight line:

$$\tan \alpha = k = 8.1 \times 10^{-8} \text{ g cm}^{-4} \text{ s}^{-1}$$

13. The following results have been obtained in experiments with the thorium oxidation reaction $\text{Th} + \text{O}_2 = \text{ThO}_2$ at 598 K:

$t, \text{ min}$	1	4	9	16	25	36	64
$(\Delta m/S) \times 10^6, \text{ g/cm}^2$	3	5.5	9	12	15.5	19	25
$(\Delta m/S)^2 \times 10^{12}, \text{ g}^2/\text{cm}^4$	9	18.28	81	144	240.25	361	625

What reaction mechanism can be inferred from these data? Calculate the rate constants.

Solution. Since an oxide layer forms on thorium particles in the course of the reaction, it may be assumed that the reaction rate will be determined by that of diffusion. To verify this assumption plot $\Delta m/S$ vs t and $(\Delta m/S)^2$ vs t (Fig. 50). $(\Delta m/S)^2 = f(t)$ is represented by a straight line, which means that the reaction rate is limited by that of diffusion. Consequently, the rate constant will be $k = \tan \alpha = 625/64 = 9.76 \times 10^{-6} \text{ g}^2/\text{cm}^4 \text{ min}$.

Problems

1. Studies into the rate of dissolution of alabaster, CaSO_4 , in water at 298 K have yielded the following results:

Dissolution time, h	CaSO_4 concentration (g) in 50 cm ³ of the solution	Dissolution time, h	CaSO_4 concentration (g) in 50 cm ³ of the solution
0	0.004	0	0.0270
0.083	0.0274	0.083	0.0480
0.167	0.0492	0.167	0.0632
0.200	0.0566	0.250	0.0736

The agitation speed is 2235 rpm. The liquid phase volume is 1 litre, 50 cm³ of the saturated solution contain 0.1047 g CaSO_4 at 298 K, and the CaSO_4 lump surface area is 31.55 cm². The surface layer surrounding the lump is 5×10^{-6} m thick, and its concentration equals that of the saturated solution. Determine the dissolution rate constant and the mass transfer coefficient.

2. A cell filled with water contains a benzoic acid pellet. Water always flows in the top part of the cell, and the $\text{C}_6\text{H}_5\text{COOH}$ concentration in the flow is zero. The concentration in the saturated solution is $c_s = 0.024$ mole/litre. $\text{C}_6\text{H}_5\text{COOH}$ dissolves and undergoes diffusion towards the flowing water. The experimental temperature is 298 K, the cell area is 2 cm², the distance to the section of the surface of the flowing water is 5 cm, the pellet weighs 1 g, and the diffusion coefficient is $D = 0.75 \text{ cm}^2/\text{day}$. Is this a steady process? What is the amount of benzoic acid dissolving under the above conditions per day?

3. A piece of marble with a constant surface area dissolves in one litre of 1 N HCl, the rate of dissolution within the first minute being 5 g/min. The solution is agitated at a constant speed. Determine the volume of CO_2 (measured under normal conditions) evolved within 20 min, as well as the time necessary for evolution of the same volume

of gas when an identical piece of marble is immersed into two litres of the same acid.

4. The rate of dissolution of a piece of marble with a constant surface area in 1 *N* HCl is 0.091 mg-equiv/s at the instant when the titre of the acid decreases by one fourth of its initial value. How long does it take for the concentration to drop to the above level?

5. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, dissolves in water at 298 K. The agitation speed is constant. The liquid phase volume is one litre. The surface area S is invariable and equal to 31.55 cm^2 . The diffusion coefficient is $D = 1.45 \text{ cm}^2/\text{day}$. The experimental results are as follows:

Time, min	0	5	10
Solution concentration in 50 cm^3 , g	0.027	0.048	0.063

Determine the type of flow. Calculate the concentration of the saturated solution (g) in 50 cm^3 ; $k = DS/\delta V$.

6. A copper ball is rotated in nitric acid and weighed every now and then. Its weight decreased from 4.3465 to 4.0463 g within the first second and from 4.0463 to 3.7673 g within the next second. The mean surface area was 289.93 and 276.40 cm^2 at these two instants, respectively. Assuming that the volume of the acid is rather large and its concentration remains practically constant, calculate the amount of copper to dissolve within the sixth second if the mean surface area at that instant is 225.15 cm^2 .

7. Fused benzoic acid with a surface area of 18 cm^2 is immersed into water which is agitated at a constant speed. At definite time intervals, 20 cm^3 samples were taken from the solution, and the benzoic acid concentration was determined by titration. The surface film thickness δ remained constant. The concentration of the saturated benzoic acid solution is 24.3 mmole/litre . The diffusion coefficient is $D = 0.5 \times 10^{-3} \text{ cm}^2/\text{min}$. The titration results are given below:

Sampling interval, min		12	15	13.3
Solution concentration before and after sampling, mmole/litre	0.75	2.05	3.05	5.05
Liquid phase volume, cm ³		1020	1000	980

Determine the mean value of the dissolution rate constant and the surface layer thickness.

8. A test tube containing water is brought into a room with ideally dry air at 293 K. The water evaporates but its level is maintained constant. No convective mixing takes place in the test tube. The test tube cross section is $S = 0.05 \text{ cm}^2$. The saturated vapour pressure is $P_{\text{H}_2\text{O}} = 0.023 \text{ atm}$. Calculate the coefficient of water vapour

diffusion into air if the distance between the water surface and test tube rim is 1.85 cm, and 1.94×10^{-3} mole of water evaporated within 87.5 h. Check the obtained value of D using the appropriate equation from the molecular-kinetic theory.

9. Calcined copper sulphate is lowered on a mesh into a test tube with water whose level is maintained constant and suspended at a distance of 20 cm from the water surface. The test tube cross section is 0.05 cm^2 . Water vapour diffuses from the water to the sulphate. The system temperature is 293 K. The saturated water vapour pressure is $P_{\text{H}_2\text{O}} = 0.023 \text{ atm}$. The coefficient of diffusion of water into air is $D_{\text{H}_2\text{O}} = 0.24 \text{ cm}^2/\text{s}$. As soon as the water vapour pressure near the sulphate surface becomes equal to $6 \times 10^{-2} \text{ mm Hg}$, the following reaction begins:



Calculate (a) the time it will take for the water vapour concentration at a distance of 10 cm from the water surface to become equal to that over the sulphate surface and (b) the amount of water to be absorbed by the sulphate within 10 min.

10. A reaction vessel is divided into two sections by a catalytic membrane. Gases of different composition were fed into the sections on either side of the catalytic membrane at the same pressure. Since the pressure in each section of the reaction vessel is constant, the exchange of the gases across the membrane was only by way of diffusion. The gas fed from one side contained 0.008 cm^3 of acetylene per cm^3 , and that fed from the other side was clean air. The acetylene diffusing across the membrane was washed out by the clean air and determined analytically. Determine the effective diffusion coefficient \hat{D}^* if the membrane thickness is $\delta = 1.34 \text{ cm}$, its cross section is $S = 4.52 \text{ cm}^2$, the clean air flow rate is $v = 10 \text{ cm}^3/\text{s}$, and the diffusion rate is $2.6 \times 10^{-3} \text{ cm}^3/\text{s}$.

11. Determine, analytically and graphically, the temperature dependence of hydrogen coefficient of diffusion into nitrogen, proceeding from the following data:

$T, \text{ K}$	273	288	289.2	293	373	435	483
$D, \text{ cm}^2/\text{s}$	0.647	0.743	0.737	0.80	1.05	1.61	1.92

12. Ethanol evaporates in air, its diffusion coefficient being $0.4673 \text{ cm}^2/\text{s}$ at 303 K and $0.5465 \text{ cm}^2/\text{s}$ at 323 K. Determine the coefficient of ethanol's diffusion into air at 313 K.

Multivariant Problem

The solubility of substance A in H_2O is c_{s1} at $T_1 = 298.2 \text{ K}$ and c_{s2} at $T_2 = 333.2 \text{ K}$. At a constant agitation speed (400 rpm) and constant surface area (horizontal surface), n_1 moles of substance A

Variant	Substance A	Solubility		t_1 , min	n_1 , mole	t_2 , min	n_2 , mole	V , litre
		at 298.2 K, c_{s1} , g/100 g H ₂ O	at 333.2 K, c_{s2} , mole/1000 g H ₂ O					
1	NaCl	35.92	6.33	20	5.39	65	6.15	1
2	NaCl	35.92	6.33	20	26.9	65	30.3	5
3	MgSO ₄ ·7H ₂ O	38.30	4.50	15	5.94	35	10.1	10
4	KCl	36.32	6.15	15	17.3	55	19.5	4
5	KBr	67.75	7.24	10	9.3	40	11.4	2
6	KI	146.45	10.35	5	15.6	15	25.0	3
7	K ₂ SO ₄	12.04	1.04	20	3.0	40	3.4	5
8	K ₄ Fe(CN) ₆ ·3H ₂ O	32.0	1.498	15	1.6	35	2.5	4
9	CaSO ₄ ·2H ₂ O	0.210	—	45	0.015	75	0.0193	20
10	CaSO ₄ ·2H ₂ O	0.21	—	45	0.746	75	0.0965	100
11	FeBr ₂	0.257	0.0072	9	0.0084	15	0.0114	6
12	FeBr ₂	0.257	0.0072	9	0.0224	15	0.0302	16
13	FeCl ₂	0.385	0.0436	30	0.080	12	0.065	5
14	FeSO ₄ ·7H ₂ O	29.7	3.69	4	0.38	10	0.9	2
15	CoSO ₄ ·7H ₂ O	37.8	3.32	15	10.8	45	20.2	15
16	NiSO ₄ ·7H ₂ O	39.6	3.65	10	1.2	40	3.0	3
17	CuSO ₄ ·5H ₂ O	22.29	2.38	9	4.96	27	10.4	12
18	ZnSO ₄ ·7H ₂ O	57.9	5.27	12	7.35	48	17.0	11
19	ZnSO ₄ ·7H ₂ O	57.9	5.27	12	4.5	24	8.08	8
20	CdSO ₄ · $\frac{8}{3}$ H ₂ O	77.0	3.92	17	11.60	51	24.6	14
21	BaCl ₂ ·2H ₂ O	36.9	1.94	25	14.5	50	15.7	19
22	PbBr ₂	0.974	0.0642	35	0.247	70	0.264	10
23	PbBr ₂	0.974	0.0642	35	0.0247	70	0.0264	1
24	PbBr ₂	0.974	0.0642	35	0.173	70	0.185	7
25	PbBr ₂	1.08	0.0697	35	0.25	70	0.268	7

were dissolved within constant volume V over time period t_1 and n_2 moles were dissolved under the same conditions over time period t_2 . Determine, at temperature T_1 , the mean value of the dissolution rate constant for salt A and the time necessary for the saturation of the solution with substance A to reach 35, 70, and 90%. Calculate approximately the heat of solution, proceeding from the values of solubility at two temperatures and assuming that $\gamma = 1$.

CHAPTER 27

Kinetics of Reactions in Solutions. Homogeneous and Heterogeneous Catalysis

Basic Equations and Symbols

The relationship between the rate constant of a reaction in a dilute solution and the ionic strength of the solution is given by the equation

$$\log k = \log k_0 + 2A z_A z_B \sqrt{I} \quad (27.1)$$

where

$$A = 1/\epsilon^{3/2} T^{3/2} \quad (27.2)$$

at 298 K, $A = 0.509$ for an aqueous solution, z_A and z_B stand for the charge numbers of the reacting ions, k_0 is the rate constant at infinite dilution ($\gamma = 1$), I is the ionic strength of the solution, and ϵ is the dielectric constant.

The relationship between the reaction rate constant and the electrostatic component of Gibbs' energy of the activated complex is

$$\log k = \log k'_0 - \frac{z_A z_B e^2 N_A}{\epsilon d_{AB} R T} \quad (27.3)$$

where k'_0 is the rate constant in a medium with $\epsilon = \infty$;

$$\frac{z_A z_B e^2}{\epsilon d_{AB} k T} = \Delta G^* \quad (27.4)$$

ΔG^* is the electrostatic component of Gibbs' energy of the activated complex, d_{AB} is the distance between the centres of the spherical ions constituting the activated complex, and $z_A e$, $z_B e$ stand for ion charges.

The rate of bimolecular homogeneous-catalytic reactions is expressed as

$$w = \frac{k_1 k_2 [A][B]}{k_2 + k_3 [B]} [K] \quad (27.5)$$

For $k_2 \gg k_3$

$$w = \frac{k_1 k_3}{k_2} [A] [B] [K] \quad (27.6)$$

For $k_2 \ll k_3$

$$w = k_1 [A] [K] \quad (27.7)$$

In highly acidic solutions, some reactions are catalyzed only by hydroxonium ions, and the expression for the reaction rate may take the following form:

$$w = k_{H^+} [H_3O^+] [S] \quad (27.8)$$

where k_{H^+} is the acid catalysis rate constant, $[H_3O^+]$ is the catalyst concentration, and $[S]$ is the concentration of the substrate. The value of the catalytic constant k_{H^+} for these ions is determined by the changes in the reaction rates in acidic solutions at different concentrations of H_3O and S .

In highly alkaline solutions,

$$w = k_{OH^-} [OH^-] [S] \quad (27.9)$$

The catalytic constant k_{OH^-} is determined by measuring the reaction rates in alkaline solutions at different concentrations of OH^- and S . If catalysis may be performed by both ions H^+ and OH^- and if the reaction proceeds in two directions at a time, the reaction rate can be written as

$$w = k_0 [S] + k_{H^+} [H_3O^+] [S] + k_{OH^-} [OH^-] [S] \quad (27.10)$$

where k_0 is the rate constant for the noncatalyzed reaction. Therefore, the first-order reaction rate constant can be expressed as

$$k = k_0 + k_{H^+} [H_3O^+] + k_{OH^-} [OH^-] \quad (27.11)$$

The reaction rate constant k in the case of acid catalysis is related to the dissociation constant K_a by Brönsted's equation

$$k = G_a K_a^\alpha \quad (27.12)$$

in which G_a and α are constants usually less than unity. For base catalysis, Brönsted's equation takes the form

$$k = G_b K_b^\beta = G'_b K_a^\beta \quad (27.13)$$

where G_b , G'_b , and β are constants.

Any reaction between gaseous substances, proceeding on a catalyst surface, can be divided into five sequential steps: (1) application of the substance to the catalyst surface, (2) adsorption of the substance, (3) reaction on the catalyst surface, (4) desorption of the reaction product from the catalyst surface, and (5) transfer of the reaction products from the catalyst surface into the gas phase. The

overall rate of the process is determined by its slowest step. If the reaction on the catalyst surface itself is the slowest step, the kinetic equation can be derived by solving a differential equation of the following general type:

$$w = \frac{\partial^2 x}{\partial t \partial S} = f(k_s, b_i, P_i) \quad (27.14)$$

where w is the reaction rate expressed as the number of moles of the substance reacting on the surface within the time interval t , k_s is the surface reaction rate constant, b_i stands for the adsorption coefficients of the substance, and P_i is the partial pressure of the reactant in different parts of the reaction zone.

In the case of monomolecular reactions in flow at a constant pressure, Eq. (27.14) takes the form (according to Frost and Balandin)

$$\bar{v} \ln \frac{1}{1-y} = \alpha + \beta \bar{v} y \quad (27.15)$$

Where \bar{v} is the speed at which the initial substance is brought to the catalyst surface, expressed in moles per unit time per unit catalyst volume, y is the degree of transformation, α is a constant directly proportional to the total catalyst surface area and the surface reaction rate constant, and β is a constant characterizing the adsorption coefficients of the substance. The coefficients α and β are the kinetic characteristics of the reaction.

The Frost-Balandin equation (27.15) can be represented graphically (Fig. 51). Plotting $\bar{v} y$ versus $\bar{v} \ln \frac{1}{1-y}$ gives a straight line. Its slope determines the value of β , while the y intercept at $y = 0$ determines that of α .

Exercises

1. Studies into the kinetics of the reaction



have yielded the following relationship between the rate constant k and ionic strength I of the solution:

I	2.34	5.61	8.10	11.22	11.73	16.90
$(5 + \log k)$	1.7640	1.7130	1.6800	1.6467	1.6418	1.5990

Calculate the rate constant k_0 at zero ionic strength.

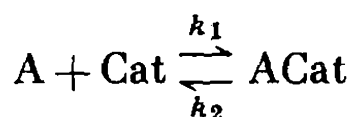
Solution. Plot $\log k$ versus \sqrt{I} and extrapolate to $\sqrt{I} = 0$ (Fig. 52):

$(5 + \log k)$	1.7640	1.7130	1.6800	1.6467	1.6418	1.5990
\sqrt{I}	1.53	2.37	2.85	3.35	3.42	4.11

The value resulting from extrapolation is $(5 + \log k_0) = 1.858$; $k_0 = 7.21 \times 10^{-4}$.

2. Use the steady concentration method to derive the equation for the rate of the homogeneous catalytic reaction $A + B + \text{Cat} \rightarrow C + \text{Cat}$ which involves the following steps:

(1) formation of intermediate product ACat as a result of reversible interaction between the catalyst and one of the reactants:



(2) formation of an activated complex as a result of interaction

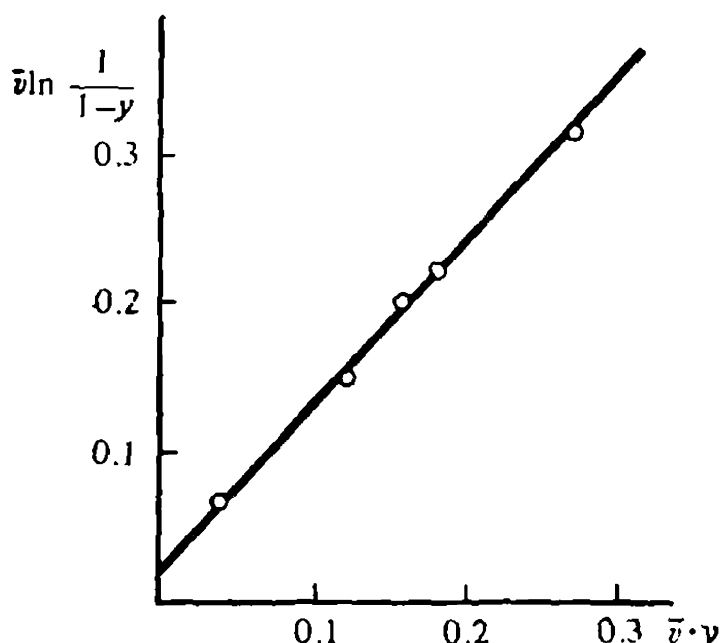


Fig. 51. $\bar{v} \ln \frac{1}{1-y}$ versus $\bar{v}y$ for the reaction of catalytic dehydration of ethanol

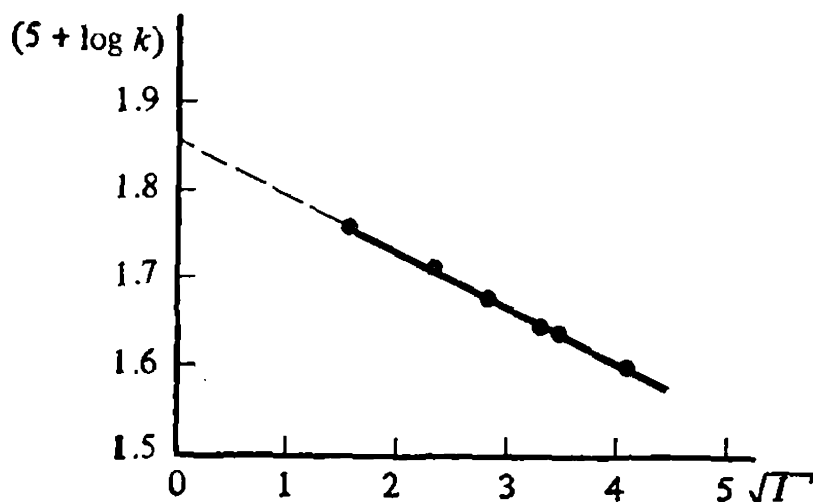
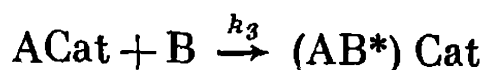
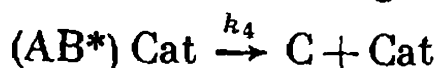


Fig. 52. $\log k$ versus \sqrt{I} for the reaction $\text{Co}(\text{NH}_3)_5\text{NO}_2^+ + \text{OH}^- \rightarrow \text{Co}(\text{NH}_3)_5\text{OH}^{2+} + \text{NO}_2^-$

between the above intermediate product and the second reactant:



(3) formation of the end products and regeneration of the catalyst:



Solution. According to the activated complex theory, the reaction rate is determined by that of dissociation of the complex into the end products:

$$\frac{d[C]}{dt} = k_4 [(AB^*) \text{Cat}] \quad (1)$$

Determine the content of the activated complex $(AB^*)\text{Cat}$ by the steady concentration method. After some time has elapsed since the process began, the rate of accumulation of the activated complex will be

$$\frac{d[(AB^*) \text{Cat}]}{dt} = k_3 [\text{ACat}] [B] - k_4 [(AB^*) \text{Cat}] = 0 \quad (2)$$

Consequently,

$$[(AB^*) \text{Cat}] = \frac{k_3}{k_4} [\text{ACat}] [B] \quad (3)$$

Express the concentration of the intermediate product in terms of those of the reactants. According to the above scheme, the reaction of accumulation of intermediate product ACat is reversible, and

$$\frac{d[\text{ACat}]}{dt} = k_1 [A] [\text{Cat}] - k_2 [\text{ACat}] - k_3 [\text{ACat}] [B] = 0 \quad (4)$$

Hence,

$$[\text{ACat}] = \frac{k_1 [A] [\text{Cat}]}{k_2 + k_3 [B]} \quad (5)$$

Substitution of Eq. (5) into Eq. (3) and the derived expression into Eq. (1) gives

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A] [B]}{k_2 + k_3 [B]} [\text{Cat}]$$

It can be seen that the reaction rate is directly proportional to the catalyst concentration.

3. $\text{C}_2\text{H}_5\text{OH}$ dissociates into ethylene and water at 653 K on 10 cm^3 of the catalyst Al_2O_3 . The consumption n of the 64% alcohol solution and the volume V_{exp} of the gas evolved within 3 min as a result of the reaction will be as follows:

$n, \text{ cm}^3$	0.144	0.65	0.937	1.15	2.37
$V_{\text{exp}}, \text{ cm}^3$	30.3	85.7	119	131.5	217

The barometric pressure is 100 121.63 Pa, and the room temperature is 300 K. Calculate the coefficients α and β in Eq. (27.15) and write the empirical equation.

Solution. To obtain the coefficients α and β in the Frost-Balandin equation $\bar{v} \ln [1/(1 - y)] = \beta \bar{v} y + \alpha$ plot a graph. To this end, calculate the values of \bar{v} , y , $\bar{v} y$, and $\ln \frac{1}{1-y}$ and plot $\bar{v} \ln \frac{1}{1-y}$

versus $\bar{v}y$ (see Fig. 51). For one experiment calculate

$$\bar{v} = \frac{m_{\text{C}_2\text{H}_5\text{OH}}}{tV_{\text{cat}}}$$

where $m_{\text{C}_2\text{H}_5\text{OH}} = ndb/M100$, b being the percentage alcohol content and $d_{\text{C}_2\text{H}_5\text{OH}} = 0.9 \text{ g/cm}^3$. Then,

$$m_1 = \frac{0.144 \times 0.9 \times 64}{46 \times 100} = 0.0018 \text{ mole}$$

$$\bar{v}_1 = \frac{0.0018}{3 \times 10} = 0.006 \text{ mmole cm}^{-3} \text{ min}^{-1}$$

Reduce the evolved gas volume to normal conditions:

$$V = \frac{V_{\text{exp}} (P_{\text{bar}} - P_{\text{H}_2\text{O}}) T_0}{P_0 (T_0 + t_{\text{room}})} \quad (P_{\text{H}_2\text{O}} = 3212.63 \text{ Pa})$$

Find the volume of C_2H_4 for this experiment under normal conditions:

$$V = \frac{30.3 \times 100 \times 121 \times 273}{760 \times 296 \times 133.3} = 27.7 \text{ cm}^3$$

Hence, the number of moles of ethylene will be

$$m_{\text{C}_2\text{H}_4} = \frac{V}{22.4} = \frac{27.7 \times 10^{-3}}{22.4} = 0.0012 \text{ mole}$$

Consequently,

$$y = \frac{m_{1, \text{C}_2\text{H}_4}}{m_{1, \text{C}_2\text{H}_5\text{OH}}} = \frac{0.0012}{0.0018} = 0.667$$

and

$$\bar{v}y = 0.060 \times 66.7 \times 10^{-2} = 0.040$$

$$\bar{v} \ln \frac{1}{1-y} = 0.0060 \ln \frac{2}{1-0.663} = 0.0060 \ln \frac{1}{0.33}$$

$$= 0.0060 \ln 3 = 0.0060 \times 1.0986 = 0.0066$$

For all experiments, the application speed and degree of transformation will be as follows:

\bar{v}	0.0060	0.0272	0.0392	0.0482	0.0995
$y \times 10^{-2}$	66.7	41.7	40.2	36.5	26.6
$\bar{v}y$	0.0040	0.0114	0.0157	0.0176	0.0264
$\bar{v} \ln \frac{1}{1-y}$	0.0066	0.0146	0.0200	0.0218	0.0306

The plot gives the following values: $\alpha = 0.012$ and $\beta \cong 1$. The equation will take the form

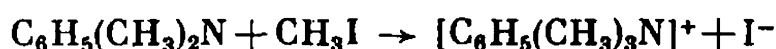
$$\bar{v} \ln \frac{1}{1-y} = \bar{v}y + 0.012$$

Problems

1. Determine the rate constant of the reaction $\text{CH}_3\text{Br} + \text{KI} = \text{CH}_3\text{I} + \text{KBr}$ in water at 298 K if the pre-exponential factor is $1.7 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ and the activation energy is 76.6 kJ/mole.

2. Determine the rate constant of the reaction $\text{CH}_3\text{Br} + \text{KI} = \text{CH}_3\text{I} + \text{KBr}$ in CH_3OH at 298 K if the pre-exponential factor is $2.3 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ and the activation energy is 76.2 kJ/mole. Compare the rate of the reaction in water, if the pre-exponential factor is $1.7 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ and the activation energy is 76.6 kJ/mole, with that of the reaction in methanol.

3. Determine the rate constant of the reaction



in nitrobenzene, dichloroethane, and benzyl alcohol at 353 K, proceeding from the values of the pre-exponential factors and activation energies given in the handbook. In which of these solvents will the reaction rate be maximum?

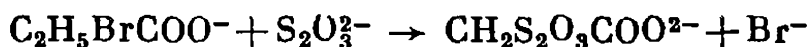
4. Given the rates of saponification of ethers in aqueous solutions (handbook), determine which of the ethers— $\text{CH}_3\text{COOC}_2\text{H}_5$, $\text{CH}_3\text{COOC}_3\text{H}_7$, or $\text{CH}_3\text{COOC}_4\text{H}_9$ —will undergo saponification at the fastest rate at 323 K. In what ratio are the saponification rate constants for these ethers?

5. Determine the time of half-conversion during saponification of 0.05 M ethyl acetate with 0.05 M aqueous solution of LiOH at 298 K, proceeding from the saponification rate constants given in the handbook.

6. Determine the time of half-conversion during saponification of ethyl acetate with an aqueous solution of NaOH, containing 0.0500, 0.0250, and 0.0125 mole/litre NaOH and equal amounts of ethyl acetate, at 298 K. Find the rate constants in the handbook.

7. Compare the initial rates of saponification of 0.05 M ethyl acetate at 298 K with 0.05 M aqueous solutions of LiOH, NaOH, and KOH.

8. Determine the change in the rate constant of the reaction



if the ionic strength of the solution varies from 0.01 to 0.04.

9. The rate constant of the reaction between sodium persulphate and iodine depends on the ionic strength as follows:

I , mole/litre	0.00245	0.00365	0.00445	0.00645	0.00845	0.011245
k , litre mole ⁻¹ s ⁻¹	1.05	1.12	1.16	1.18	1.26	1.39

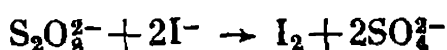
Represent these data graphically using Eq. (27.1) and calculate $z_A z_B$. What is the charge on the persulphate ion if the step controlling the reaction rate is the interaction between the persulphate and iodine ions? Explain why the charge product $z_A z_B$ is not an integer.

10. One of the results of an experiment with the reaction



is that, when the ionic strength of the solution is 5.61, the rate constant of this reaction equals 5.164×10^{-4} . Determine the rate constant of the reaction at zero ionic strength.

11. How will the rates of the reactions



be affected by an increase in (a) the dielectric constant, (b) the ionic strength of the solution, and (c) the hydrostatic pressure? Determine the sign of entropy for each reaction.

12. Calculate the electrostatic component of ΔG^\ddagger , ΔH^\ddagger , and $T\Delta S^\ddagger$ (kJ/mole) if $z_A z_B = -2$, $\epsilon = 80$, $(\partial \ln \epsilon / \partial T)_P = -0.0046$, and $d_{AB} = 25$ nm at 298 K.

13. The rate constant of hydrolysis of diazo-acetic ester



varies with the concentration of H^+ ions as follows:

$[\text{H}_3\text{O}^+]$, mole/litre	0.00046	0.00087	0.00158	0.00323
k , litre mole ⁻¹ s ⁻¹	0.0168	0.0320	0.0578	0.1218

Represent these data graphically and determine the rate constant of catalysis by hydrogen ions (k_{H^+}).

14. The mutarotation of glucose is a first-order reaction with respect to the glucose concentration and is catalyzed by acids (A) and bases (B). The first-order rate constant can be expressed using an equation of the same type as in the case of reactions proceeding along several parallel paths:

$$k = k_0 + k_{\text{H}^+} [\text{H}^+] + k_A [\text{A}] + k_B [\text{B}]$$

where k_0 is the first-order rate constant in the absence of any acids and bases (with the exception of water). The following results have been obtained for this reaction at 291 K in a medium containing 0.02 mole/litre sodium acetate and acetic acid in different concentrations:

$[\text{CH}_3\text{COOH}]$, mole/litre	0.020	0.105	0.199
$k \times 10^4$, min ⁻¹	1.36	1.40	1.46

Calculate k_0 and k_A . The term with k_{H^+} is negligibly small under these conditions.

15. The rate constant of hydrolysis of diazo-acetic ester varies with the concentration of H^+ ions as follows:

c_{H^+} , mole/litre	0.00046	0.00087	0.00158	0.00323
k , litre mole $^{-1}$ s $^{-1}$	0.0168	0.0320	0.0578	0.1218

(the reaction being of the first order with respect to the ester). Determine the mean rate constant of catalysis by H^+ ions.

16. The mutarotation of glucose is catalyzed by acids and bases and is of the first order with respect to the glucose concentration. If perchloric acid is used as the catalyst, the concentration of H^+ ions may be considered equal to that of perchloric acid, and the effect of the perchlorate ion may be ignored because it is an extremely weak base. The following values of the first-order rate constants have been obtained:

$[HClO_4]$, mole/litre	0.0010	0.0480	0.0099	0.0192	0.0300	0.0400
$k \times 10^4$, min $^{-1}$	1.25	1.38	1.53	1.90	2.15	2.59

Determine the constants k_0 and k_{H^+} .

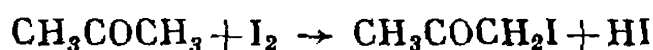
17. A solution containing 0.5 mole/litre acetic acid and 0.3 mole/litre sodium acetate has been prepared. The acetic acid dissociation constant is 1.8×10^{-5} , and the exponent α in Brönsted's equation for the acid catalysis reaction is 0.9. Calculate the percentage reaction intensity in terms of hydrogen ions, acetic acid, and water.

18. Listed below are acid dissociation constants and catalytic constants for the reaction of nitroamide dissociation promoted by some basic ions:

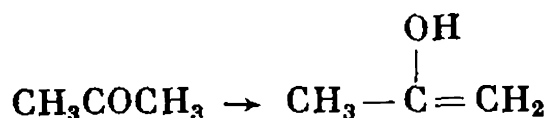
Ion	K_a	k	Ion	K_a	k
Hydroxyl	1.1×10^{-16}	1×10^6	Benzoate	6.5×10^{-5}	0.189
Trimethyl acetate	9.4×10^{-6}	0.822	Formate	2.1×10^{-4}	0.082
Propionate	1.4×10^{-5}	0.649	Monochloroacetate	1.4×10^{-3}	0.016
Acetate	1.8×10^{-5}	0.504	<i>o</i> -Nitrobenzoate	7.3×10^{-3}	0.0042
Phenyl acetate	5.3×10^{-5}	0.232	Dichloroacetate	5.0×10^{-2}	0.0007

Represent these data graphically in such a manner as to demonstrate the applicability of Brönsted's equation and determine the constants of the equation.

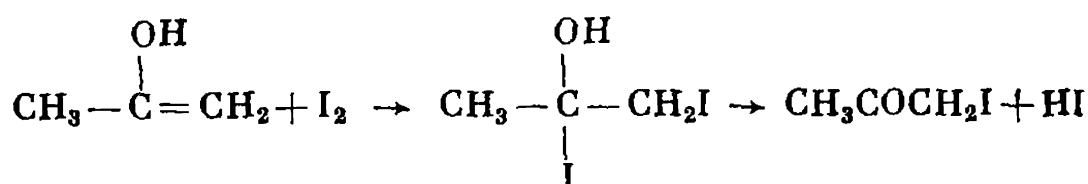
19. The reaction between acetone and iodine is



The reaction may be regarded as involving preliminary enolization of acetone:



with subsequent attachment of iodine and detachment of a hydrogen iodide molecule:



This mechanism is corroborated by the reaction rate being independent of the iodine concentration and remaining the same when bromine is substituted for iodine. Therefore, enolization is the step determining the reaction rate, whereas the subsequent attachment of the halogen is a fast step. Proceeding from the acetone iodination rate constants tabulated below:

Catalyst	K_a	$k \times 10^6, \text{ l}/(\text{mole s})$	Catalyst	K_a	$k \times 10^6, \text{ l}/(\text{mole s})$
Dichloroacetic acid	5.7×10^{-2}	220	α -Chloropropionic acid	1.01×10^{-4}	5.9
α, β -Dibromopropionic acid	6.7×10^{-3}	63	Acetic acid	1.75×10^{-5}	2.4
Monochloroacetic acid	1.41×10^{-3}	34	Propionic acid	1.34×10^{-5}	1.7
Glycolic acid	1.54×10^{-4}	8.4	Trimethylacetic acid	9.1×10^{-3}	1.9

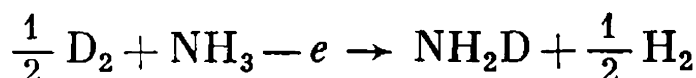
calculate the mean values of the coefficients in Brönsted's equation and the catalytic constants of all acids.

20. Brönsted's equation for the reaction of acetone iodination in the presence of acids with $p = q = 1$ (q being the number of positions in the catalyzing base capable of accepting a proton, and p being the number of protons capable of detachment in the acid conjugated with the base) takes the form $k = 7.90 \times 10^{-4} K_a^{0.62}$. Calculate the catalytic rate constant k in the presence of monochloroacetic acid and compare the result with the experimental value $k_{\text{exp}} = 34 \text{ litre mole}^{-1} \text{ s}^{-1}$. The monochloroacetic acid dissociation constant is $K_a = 1.41 \times 10^{-3}$.

21. How many times will the rate of a hypothetical gaseous reaction increase at 400 K if a solid catalyst is introduced into the kinetic system? The activation energy of the reaction without the catalyst

is $E_g = 29\,824$ J/mole, and that of the reaction with the catalyst is $E_{g-\text{cat}} = 26\,000$ J/mole. The pre-exponential factors of the Arrhenius equation are the same in both cases: $k_{0g} = k_{0g-\text{cat}}$.

22. The catalytic exchange between deuterium and ammonia proceeds as follows:



Given below are the values of the activation energy of the reaction on various catalysts and the energy of electronic work function of the metallic catalyst:

Metal	Pt	Ni	Pd	Fe	Ag	Cu
Activation energy E_a , kJ/mole	21.6	39.0	38.0	51.0	60.0	58.0
Electronic work function ϕ , kJ/mole	518	483	481	456	438	437

Derive the equation relating the activation energy of the above reaction to the energy of electronic work function of the metal and determine the change (as the ratio) in the rate of the reaction on the above metals as compared to platinum. The pre-exponential factor of the Arrhenius equation is the same for all metals.

23. The activation energy of the ammonia dissociation reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ without a catalyst is $E_g = 326$ kJ/mole, and when the reaction proceeds on catalysts W, Mo, Fe, and Os at the same temperature, the activation energies are $E_W = 163$ kJ/mole, $E_{\text{Mo}} = 121.3$ kJ/mole, $E_{\text{Fe}} = 125.5$ kJ/mole, and $E_{\text{Os}} = 197$ kJ/mole, respectively. Determine the relationship between the "true" activation energy of the heterogeneous reaction and the heat of adsorption of the initial substances. Calculate the heat of adsorption of the activated complex on the catalyst.

24. Ethanol dissociates on the catalyst Al_2O_3 according to the equation $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. At 650 K, the effective rate constant is 2.34 s^{-1} . The temperature dependence of the surface reaction rate constant is given by the equation $\log k = 6.06 - 4230/T$. Determine the activation energy of the surface reaction and the diffusion rate constant.

25. The kinetics of dissociation of formic acid $\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$ on various catalysts at 473 K is characterized by the following data:

Catalyst	Glass	Au	Ag	Pt	Rh
Activation energy, kJ/mole	103	98	130	92	146
Relative reaction rate	1	40	40	2000	10 000

The dissociation rates are related to equal catalyst surface areas. Explain the difference in the rates.

26. Oleic acid dissolved in acetic acid undergoes hydrogenation at 320 K in the presence of a platinum catalyst. The hydrogenation rate varies as follows, depending on the catalyst:

w , mg/min	3.7	7.4	11.3	14.9
Amount of catalyst, g	0.025	0.05	0.0625	0.10

The shaking rate is 600 oscillations per minute. Define the hydrogenation region in which the above reaction proceeds.

27. The relationship between the rate of hydrogenation of an alcohol in glacial acetic acid with vigorous shaking (500-600 oscillations/min) at 290 K in the presence of a platinum catalyst and the amount of the latter is linear, which is typical of the kinetic region. Proceeding from the following data:

Amount of catalyst, g	0.03	0.06	0.06	0.09	0.15	0.24	0.30	0.40	0.50
w , cm ³ /s	1.56	3.83	3.75	6.04	9.75	13.5	18.2	22.7	37.6

plot the reaction rate constant versus the amount of catalyst (metallic platinum, in g). The Pt content in the catalyst is 6%.

28. The reaction $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$ proceeds at 693 K on Al_2O_3 . The degree of filling of the catalyst with the initial substance is given below as a function of pressure:

Degree of filling	0.0715	0.1334	0.1876	0.235	0.278	0.316	0.350	0.381	0.409	0.435
Pressure, mm Hg	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0

Calculate the effective and true reaction rate constants if the reaction products do not slow down the process.

29. Studies into the kinetics of homomolecular oxygen exchange on gadolinium oxide at temperatures ranging from 78 to 500 °C have yielded the following reaction rate constants at different temperatures:

T , K	233	273	300	473	673
$k \times 10^5$, s ⁻¹	0.177	0.0224	0.0955	4.48	27.16

Plot the $\log k = f(1/T)$ curve and determine the activation energy in the temperature ranges of 573 to 300 and 300 to 223 K. Explain why the activation energy is negative.

30. Derive the equation for dehydration of ethanol (in flow) over aluminium oxide at 653.2 K if

\bar{v}	0.060	0.152	0.272	0.331	0.392	0.423	0.482	0.542	0.995	1.464
$y \times 10^2$	66.7	55.0	41.7	42.8	40.2	40.1	36.5	37.1	26.6	22.1

31. In an experiment with dehydration of ethanol, $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ on the catalyst Al_2O_3 at 653 K, the rate of consumption n of the 75% water-alcohol solution and the volume V_{exp} of

the gas trapped in the gas burette were measured every three minutes with the following results:

$n \times 10^6, \text{ m}^3$	0.2	0.31	0.41	0.62	0.82	1.06	1.37	1.66	1.95
$V_{\text{exp}} \times 10^6, \text{ m}^3$	61	84.2	107.5	143	177	218	263	283	302

Calculate the coefficients α and β in the Frost-Balandin equation for this reaction under the above conditions if the catalyst volume is 15 cm^3 , the experimental temperature is 293.2 K , and the barometric pressure is $99\,641.7 \text{ Pa}$ (747.5 mm Hg).

CHAPTER 28

Kinetics of Electrochemical Reactions

Basic Equations and Symbols

The electric charge required for dissociation of 1 g-equiv of an electrolyte equals 96 450 coulombs and is known as the Faraday constant. The amount m of the substance that has undergone dissociation, deposited on the electrodes, or formed in solution as a result of electrolysis is calculated using the equation

$$m = \frac{zIt}{F} \quad (28.1)$$

in which z is the equivalent weight, in g; I is the current intensity, in A; t is time, in s; and F is the Faraday constant.

During electrolysis, part of the current is spent in side processes, which is why the practical yield of electrolysis is always below the theoretical value. The yield is usually calculated in terms of current:

$$Y_c = \frac{\text{amount of substance formed in electrolysis}}{\text{calculated amount of substance to be formed in electrolysis}}$$

Most electrolytic reactions are irreversible. The observed decomposition potential exceeds the value calculated from thermodynamic data. This overpotential depends on the area of the electrodes and the condition of their surface, the presence of impurities in the solution, and the density of the current passing through the latter.

In many electrochemical processes, the current density i and overpotential η are related by the Tafel equation

$$\eta = a + b \log i \quad (28.2)$$

where a and b stand for certain parameters characterizing the system under consideration.

Most electrochemical reactions involving organic substances have a step in which these substances undergo preliminary adsorption on the electrode surface. The rate of adsorption of organic substances

is given by the Roginsky-Zeldovich equation

$$w = kc \exp(-\alpha f' \theta'_R) \quad (28.3)$$

in which k is the adsorption rate constant, c is the organic substance concentration, α is a constant, and f is the coefficient of irregularity of the electrode surface.

The time dependence of adsorption is given by the equation

$$\theta'_B = \beta + \frac{1}{\alpha f} \ln t \quad (28.4)$$

where θ'_R is the degree of filling of the electrode surface with the organic substance.

Exercises

1. Current was passed through a CuSO_4 solution at a rate of 5 A h, and 5.6 g of copper were deposited on the electrode (cathode) ($m_{\text{act}} = 5.6$). Determine the current yield.

Solution. The equivalent weight of copper is $\frac{63.57}{2} = 31.785$ g.

The amount spent is $\frac{5}{26.8} = 0.1865$ F ($96\,540 \times 0.1865 = 18\,000$ C).

Hence, theoretically, according to Faraday's law, the amount of copper to be deposited must be

$$m_{\text{theor}} = 31.785 \times 0.1865 = 5.92 \text{ g Cu}$$

Consequently, the current yield of copper is

$$Y_C = \frac{m_{\text{act}}}{m_{\text{theor}}} 100 = 5.6/5.92 \times 100 = 94.7\%$$

2. When current is passed through slightly diluted sulphuric acid, 40 cm^3 of hydrogen evolve on the cathode within 5 min, as measured at 288 K and 748 mm Hg. Determine the current intensity through the electrolyte.

Solution. Determine the weight of the evolved hydrogen (on the cathode) using the equation $m = MPV/RT$. We have $M = 2.016$, $P = 748/760$ atm, $V = 0.04$ litre (40 cm^3), $R = 0.082$ litre-atm mole $^{-1}$ K $^{-1}$, and $T = 288$ K. Hence,

$$m = \frac{2.016 \times 748 \times 0.04}{760 \times 0.082 \times 288} = 0.00336 \text{ g H}_2$$

To determine the current intensity use the equation

$$[m = 0.00336 \text{ g}, z = 1.008, t = (5 \times 60) = 300 \text{ s}]$$

$$I = \frac{m \, 96\,540}{z t} = \frac{0.00336 \times 96\,540}{1.008 \times 300} = 1.08 \text{ A}$$

3. An iron sheet having a surface area of 1000 cm^2 is used as the cathode in electrolysis of a zinc salt. What will be the thickness of

the zinc layer deposited on the cathode within 25 min if the mean current density is 2.5 A/dm²? The density of zinc is 7.15 g/cm³.

Solution. Determine the amount of zinc deposited on the iron electrode, using the equation

$$m = zIt/F$$

To do this, calculate the equivalent weight of zinc:

$$z = \frac{65.38}{2} = 32.69 \text{ g}$$

Determine the current intensity with the aid of the equation $I = iS$

$$I = 2.5 \times 10 = 25 \text{ A}$$

The electrolysis time will be

$$t = 25 \times 60 = 1500 \text{ s}$$

The deposited amount of zinc will be

$$m = \frac{32.69 \times 25 \times 1500}{96\,500} = 12.7 \text{ g}$$

The weight and density of the deposited zinc are known. Find its volume:

$$V = \frac{12.7}{7.15} = 1.776 \text{ cm}^3$$

Calculate the thickness of the zinc layer formed on the electrode

$$\delta = \frac{1.776}{1000} = 1.776 \times 10^{-3} \text{ cm}$$

4. Studies into the kinetics of maleic acid adsorption on a smooth rhodium electrode at 293 K and a potential $\varphi = 0.2 \text{ V}$ by the electrochemical impulse methods have produced the following results:

Time, s	θ'_R at a concentration, mole/litre, of			
	10^{-2}	5×10^{-3}	2×10^{-3}	10^{-3}
5	0.06	0.03	0.01	0.01
10	0.13	0.06	0.02	0.01
20	0.19	0.12	0.03	0.02
30	0.23	0.17	0.07	0.02
50	0.27	0.21	0.14	0.04
100	0.34	0.28	0.20	0.11
200	0.42	0.34	0.26	0.18
300	0.43	0.37	0.30	0.23
500	0.44	0.39	0.33	0.28
1000	0.45	0.39	0.32	0.30

Plot the kinetic adsorption curves (θ'_R vs $\log t$), check whether the equation $w = kc \exp(-\alpha f' \theta'_R)$ can be used to describe the adsorption kinetics, and determine the adsorption rate constant.

Solution. Figure 53 represents the degree of filling (θ'_R) of the surface with chemisorbed organic particles of maleic acid versus the

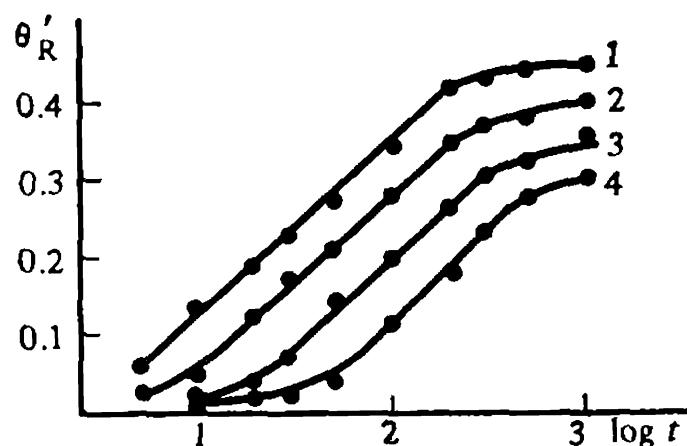


Fig. 53. Degree of filling of the surface with maleic acid of different concentrations versus adsorption time:

1— 10^{-2} mole/litre; 2— 5×10^{-3} mole/litre; 3— 2×10^{-3} mole/litre; 4— 10^{-3} mole/litre

logarithm of adsorption time, $\log t$. A clearly defined linear portion is observed for solutions of all concentrations, which is to say that the time dependence of adsorption can be given by the equation

$$\theta'_R = \beta + \frac{1}{\alpha f'} \ln t$$

in which the constant β is a function of concentration. Determine $\alpha f'$ as the slope of the straight line, which equals $1/\alpha f'$. For a maleic acid concentration of 5×10^{-3} mole/litre we have

$$\alpha f' = \frac{2.3 (\log \tau_2 - \log \tau_1)}{\theta'_{R(2)} - \theta'_{R(1)}} = \frac{2.3 \times 1}{0.275 - 0.06} = 10.7$$

Similarly, calculate $\alpha f'$ for all maleic acid concentrations. The quantity $\alpha f'$ is virtually independent of concentration and is a characteristic of adsorption of the acid on rhodium:

$$\alpha f'_{\text{mean}} = \frac{10.2 + 10.7 + 10.4 + 9.6}{9} = 10.2$$

Calculate the rate of maleic acid adsorption on rhodium for solutions of different concentrations (e.g. for $c = 10^{-2}$ mole/litre and $\theta'_R = 0.09$):

$$w = \frac{\Delta \theta'_R}{\Delta t} = \frac{\theta'_{R(2)} - \theta'_{R(1)}}{t_2 - t_1} = \frac{0.13 - 0.06}{5} = 1.4 \times 10^{-2} \text{ s}^{-1}$$

and tabulate the results as follows:

for $c = 10^{-2}$ mole/litre

θ'_R	0.09	0.16	0.21	0.25	0.30	0.38
w	1.4×10^{-2}	6×10^{-3}	4×10^{-3}	2×10^{-3}	1.4×10^{-3}	8×10^{-4}
$-\log w$	1.84	2.22	2.4	2.7	2.86	3.1

for $c = 5 \times 10^{-3}$ mole/litre						
θ'_R	0.09	0.15	0.19	0.25	0.32	0.35
w	7×10^{-3}	5×10^{-3}	2×10^{-3}	1.4×10^{-3}	6×10^{-4}	3×10^{-4}
$-\log w$	2.15	2.3	2.7	2.86	3.2	3.5
for $c = 2 \times 10^{-3}$ mole/litre						
θ'_R	0.05	0.11	0.17	0.23	0.28	
w	4×10^{-3}	3.5×10^{-3}	1.2×10^{-3}	6×10^{-4}	4×10^{-4}	
$-\log w$	2.4	2.45	2.92	3.2	3.4	
for $c = 10^{-3}$ mole/litre						
θ'_R	0.03	0.07	0.14	0.20	0.26	
w	10^{-3}	1.4×10^{-3}	7×10^{-4}	5×10^{-4}	2.5×10^{-4}	
$-\log w$	3	2.86	3.15	3.3	3.6	

Proceeding from the calculated values, plot $\log w$ versus θ'_R for the

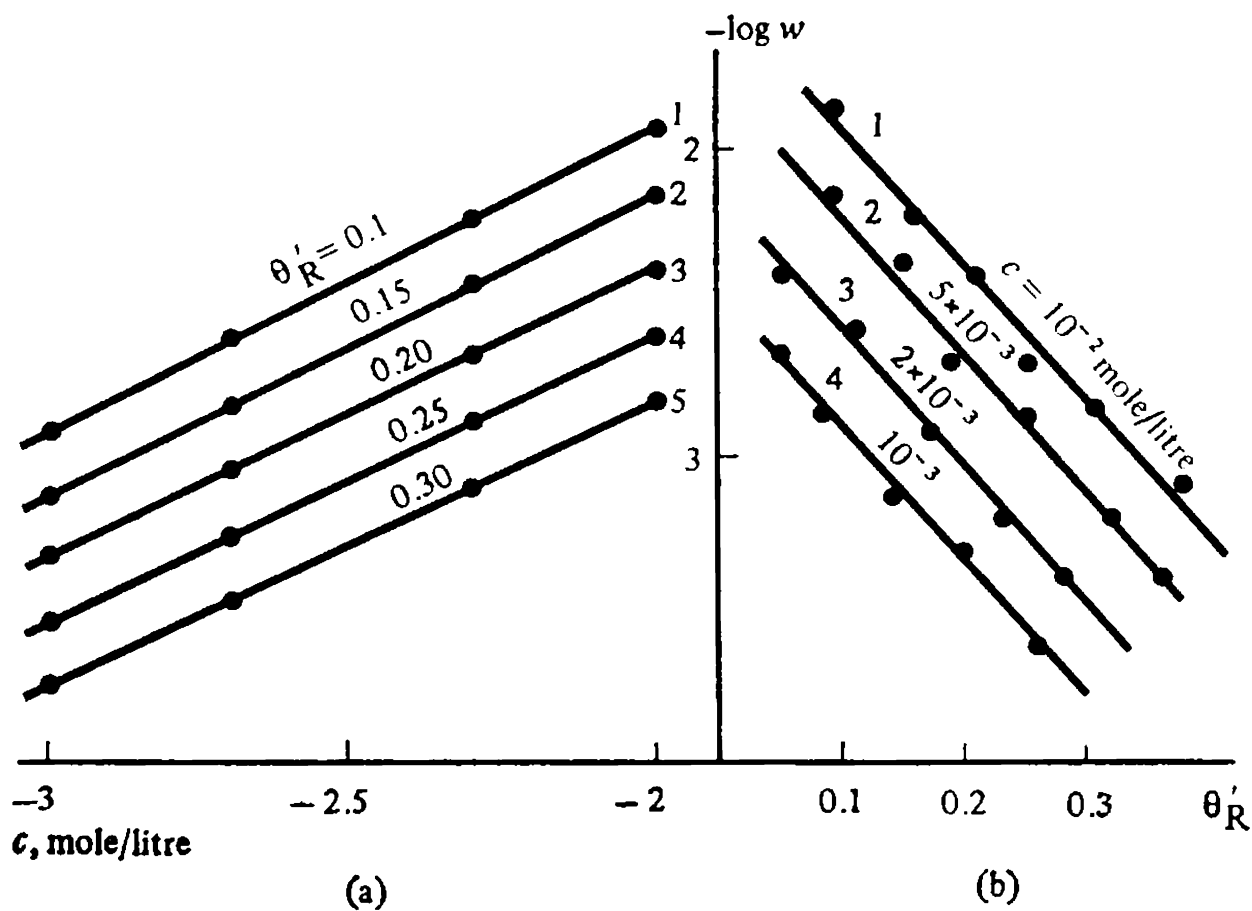


Fig. 54. Rate of maleic acid adsorption on rhodium versus concentration (a) and degree of filling of the surface (b)

solutions of the above concentrations (Fig. 54). Use the results to calculate $\alpha f'$:

$$\alpha f' = \frac{2.3 (\log w_2 - \log w_1)}{\theta_1 - \theta_2}$$
$$\alpha f'_{\text{mean}} = 10.4$$

Use the derived $\log w = f(\theta'_R)$ curve to plot $\log w$ versus $\log c$ at $\theta'_R = \text{const}$ (Fig. 54a). Taking the logarithm of the equation $w = kc^n \exp(-\alpha f' \theta'_R)$ gives

$$\ln w = \ln k + n \ln c - \alpha f' \theta'_R$$

then, at $\theta'_R = \text{const}$,

$$n = (\log w_2 - \log w_1) / (\log c_2 - \log c_1)$$

$$n_1 = 0.94, n_2 = 1.01, n_3 = 0.99, n_4 = 1.05, n_5 = 0.97$$

$$n_{\text{mean}} = 0.99 \pm 0.05$$

Thus, the exponent in the concentration term of the kinetic equation for the adsorption rate is approximately equal to unity. Calculate the adsorption rate constants:

$$k = \frac{w}{c} \text{ at } \theta'_R = 0 \text{ and } n = 1$$

To determine the adsorption rate $w_{\theta=0}$ extrapolate the relationships between $\log w$ and θ'_R (Fig. 54b) to $\theta'_R = 0$. Tabulate the extrapolated values of the adsorption rate and the adsorption rate constants corresponding to different maleic acid concentrations:

c , mole/litre	10^{-2}	5×10^{-3}	2×10^{-3}	10^{-3}
$w_{\theta'_R=0}$	3.16×10^{-2}	1.7×10^{-2}	6.3×10^{-3}	3.6×10^{-3}
k , litre mole $^{-1}$ s $^{-1}$	3.16	3.40	3.15	3.16
$k_{\text{mean}} = 3.25 \pm 0.15$				

Thus, the overall kinetic equation for the process of maleic acid adsorption on rhodium takes the form

$$w = 3.25c \exp(-10.2\theta'_R)$$

5. Studies into the adsorption of maleic acid on a rhodium electrode at different temperatures have yielded the following results:

Time, s	θ'_R at a temperature, °C, of				
	60	50	40	30	20
10	0.07	0.06	0.04	0.03	0.02
20	0.17	0.12	0.09	0.06	0.03
30	0.20	0.16	0.14	0.12	0.07
50	0.27	0.25	0.19	0.17	0.14
100	0.38	0.32	0.29	0.24	0.20
200	0.42	0.39	0.35	0.33	0.27
300	0.42	0.39	0.38	0.34	0.31
500	0.44	0.41	0.38	0.36	0.32

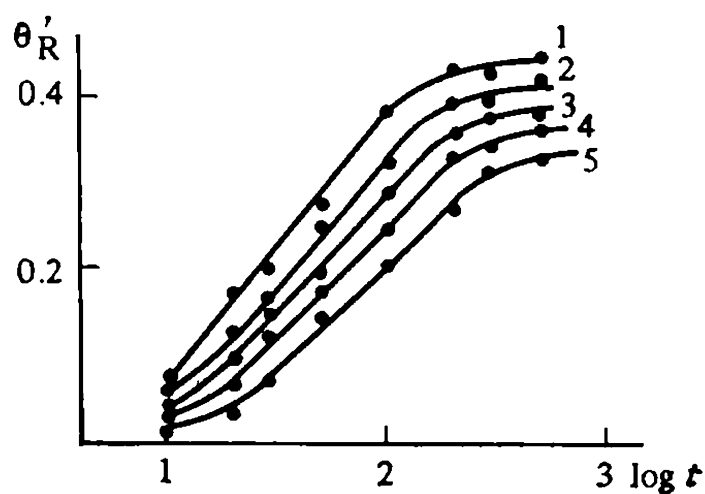


Fig. 55. Kinetic curves of maleic acid adsorption at different temperatures:
1—60 °C; 2—50 °C; 3—40 °C; 4—30 °C; 5—20 °C

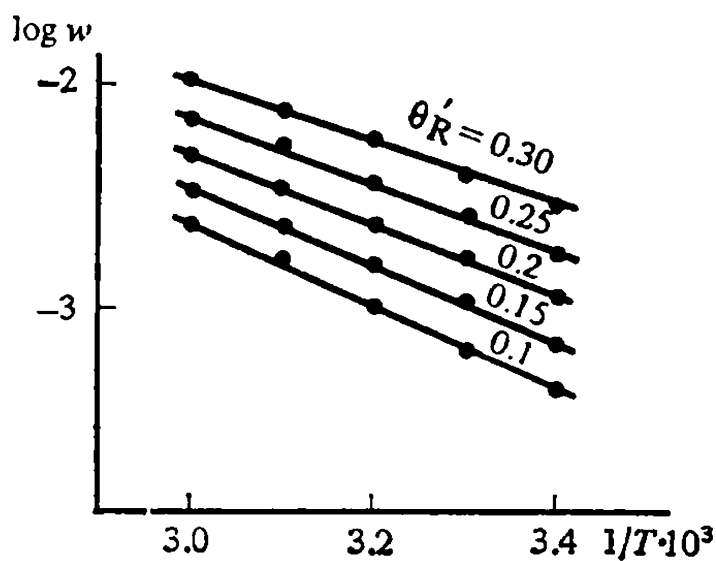


Fig. 56. Adsorption rate versus inverse temperature at different degrees of filling

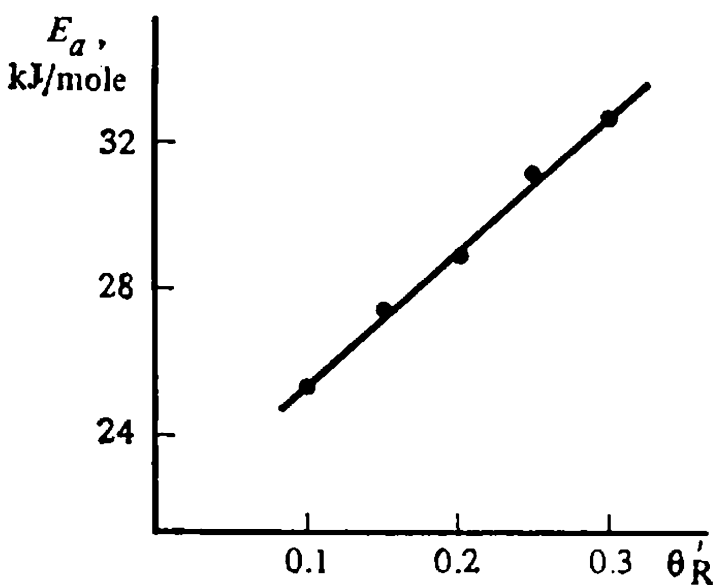


Fig. 57. Activation energy variations with the degree of filling

Determine the activation energy of maleic acid adsorption on rhodium at different degrees of filling of the surface with the adsorbed hydrogen and establish the relationship between the adsorption activation energy and the degree of filling.

Solution. Plot θ'_R versus $\log t$ at different temperatures (Fig. 55). Then determine the adsorption rate:

$$\theta'_R = 0.2, \quad t = 60^\circ\text{C}$$

$$w = \frac{0.23 - 0.17}{34.7 - 21.9} = 4.68 \times 10^{-3}$$

$$\log w = \bar{3}.67 = -2.33$$

Tabulate the calculation results:

Temperature, °C	log w at θ'_R of				
	0.10	0.15	0.20	0.25	0.30
60	-1.98	-2.17	-2.33	-2.49	-2.65
50	-2.14	-2.30	-2.47	-2.65	-2.79
40	-2.25	-2.43	-2.62	-2.80	-2.99
30	-2.41	-2.60	-2.78	-2.98	-3.21
20	-2.55	-2.76	-3.00	-3.18	-3.40

Plot $\log w$ versus $1/T$ at $\theta'_R = \text{const}$ (Fig. 56) proceeding from the results which are used to determine the adsorption activation energy:

$$E_a = 2.3R \tan \alpha, \quad \text{where } \tan \alpha = \frac{\Delta \log w}{\Delta 1/T}$$

Plot the activation energy versus the degree of filling θ'_R (Fig. 57). This relationship is linear and is given by the equation $E_a = E_0 + \alpha' RT \theta'_R$, where $E_0 = 23.9 \text{ kJ}$.

Problems

1. 1.5 A current passes through a copper sulphate solution. Determine the theoretical yield of copper over a period of one hour.

2. Water is electrolyzed to produce 0.6 litre of oxyhydrogen gas at 293 K and 740 mm Hg. How long will the process take if the current intensity is 2 A?

3. A metal object is to be coated with a nickel layer 0.3 mm thick. The surface area of the object is 100 cm^2 . The density of nickel is 9.0 g/cm^3 . How long will it take to pass 3 A current if the current yield is 90%?

4. Determine the current requirements to produce one tonne of copper at a current yield of 96%.

5. Electrolysis of a 20% potassium acetate solution at 290 K yields, among other things, ethane evolved on the anode according to the equation



The ratio between the molecules of ethane evolved on the anode and those of hydrogen evolved on the cathode is 0.8. Determine the current yield of ethane.

6. To reduce nitrobenzene to aniline, 20 g $\text{C}_6\text{H}_5\text{NO}_2$, 30 cm³ of an alcohol, 250 cm³ of water, 11 g HCl, and 1 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were placed in the cathode space. After passing current at a rate of 26.5 A h through the lead-cathode electrolytic cell, 12.76 g of aniline were produced. Determine the current yield.

7. Current is passed successively through vessels with aqueous solutions of AgNO_3 , CuSO_4 , KI, and HClO_4 . Which substances and in what amounts will be deposited on platinum electrodes in CuSO_4 , KI, and HClO_4 solutions if 0.1079 g of silver was deposited on the cathode in the vessel containing the AgNO_3 solution?

8. When current is passed through a nickel sulphate solution, nickel and hydrogen evolve on the cathode. Determine the current yield of nickel if 17.4 cm³ H_2 evolved (under normal conditions) after passing current at a rate of 0.5 A h.

9. If the cathode space is separated from the anode one during electrolysis of a common salt solution, sodium hydroxide is produced in the former and chlorine on the anode. Write the equations for the electrode reactions and determine the current yield of the alkali if after six hours of electrolysis with 1000 A current 70.5 litre of the cathodic solution contained 118 g of sodium hydroxide per litre of the solution.

10. Electrolysis of a concentrated acidic solution of ammonium sulphate yields ammonium persulphate on the anode at a low temperature. Write the equation for the anodic reaction and define the current requirements for producing 1 kg of ammonium persulphate if the current yield of the product is 75%. What by-product and in what amount will evolve on the anode?

11. Plot the potential shift versus the density of the polarizing current during electrolysis of a solution containing 0.01 mole/litre CuSO_4 and 1 mole/litre H_2SO_4 . The diffusion coefficient of Cu^{2+} ion is $D_{\text{Cu}^{2+}} = 1 \times 10^{-5} \text{ m}^2/\text{s}$ and the diffusion layer thickness is $\delta = 10 \text{ }\mu\text{m}$ at 298 K.

12. When a solution is agitated under a given set of conditions, the limiting current of copper deposition from 0.02 M CuSO_4 has the density $i_{\text{lim}} = 20 \text{ mA/cm}^2$. Calculate the copper electrode potential (with respect to the normal hydrogen electrode) at cathode cur-

rent densities of 5, 10, 15, 18, and 19 mA/cm² if merely concentration polarization takes place ($\gamma_{\pm\text{CuSO}_4} = 0.317$, 298 K).

13. The potential of a cadmium cathode ($\varphi_c = -0.535$ V) varies in a 0.01M CdSO₄ solution ($\gamma_{\pm} = 0.399$). Determine which part of the limiting current is constituted by the current at a given potential if the polarization during cadmium deposition is a merely concentration one. Find the ratio between this current and the limiting current for $\varphi_c = -0.505$, -0.490 , -0.485 , and -0.480 V (298 K).

14. A silver-copper alloy is deposited from cyanide electrolytes containing 8 g/litre of copper and 2 g/litre of silver in the form of Cu(CN)₂ and Ag(CN)₂ ions (calculated as metals). Determine the weight percentage of the alloy if the deposition of both metals is conducted at the limiting currents and the ionic diffusion coefficients are the same.

15. An electrolyte contains 10 g/litre of nickel and 5 g/litre of cobalt as sulphates. Determine the current yield of their alloy, the weight of the deposit and its composition if electrolysis proceeds at a current density of 20 A/dm² for 20 min on an electrode having a surface area of 10 cm² and both metals are deposited at the limiting current. Assume that the mass transfer coefficients D/δ for ions Ni²⁺ and Co²⁺ are the same and equal to 1.6×10^{-3} cm/s.

16. The kinetics of hydrogen evolution was studied on a single crystal of Ni with a (III) face in 0.1M KOH, pH 13.15, at 293 K. The following results have been obtained:

η , V	0.075	0.114	0.150	0.190	0.225	0.265	0.300
$\log i$ [A/cm ²]	-4.00	-3.80	-3.60	-3.40	-3.20	-3.00	-2.80

Calculate the constants a , b , and α in the Tafel equation.

17. The kinetics of hydrogen evolution on single crystals of Cu was studied in a highly acidic solution with the following results:

η , V	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65
$i_{20}^\circ\text{C}$, A/cm ²	0.0115	0.0190	0.044	0.11	0.305	0.77	1.65	3.0
$i_{30}^\circ\text{C}$, A/cm ²	0.0162	0.29	0.073	0.195	0.535	1.28	2.55	4.25
$i_{40}^\circ\text{C}$, A/cm ²	0.022	0.044	0.11	0.29	0.75	1.72	3.15	5.2
$i_{50}^\circ\text{C}$, A/cm ²	0.037	0.072	0.19	0.51	1.15	2.5	4.3	6.6

Determine the constants a and b in the Tafel equation at all temperatures. Use the experimental data to plot the $\log i$ vs $1/T$ curves at $\eta = \text{const}$. Determine the effective activation energy.

18. Calculate the current yield of nickel in electrolysis of a nickel sulphate solution with $a_{\text{Ni}^{2+}} = 0.1$ at pH 3 and pH 6 if the cathode potential with respect to the normal hydrogen electrode is $\varphi = -0.80$ V. No depolarization and superpolarization effects are observed in the nickel-hydrogen system, the constant a in the Tafel equation for the overvoltage of hydrogen evolution on nickel at pH 0 is 0.62 V, the standard exchange current of the nickel electrode

is $i_{0,\text{Ni}} = 3 \times 10^{-8} \text{ A/cm}^2$, and the transfer coefficients for the discharge of the H^+ and Ni^{2+} ions are $\alpha_{\text{H}^+} = 0.5$ and $\alpha_{\text{Ni}^{2+}} = 0.29$;

$$b_{\text{Ni}^{2+}} = \frac{2.3RT}{\alpha z F} = 0.100 \text{ V}, \quad \varphi_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.25 \text{ V}, \quad T = 303 \text{ K}$$

19. Studies into the adsorption of maleic acid on platinum at 293 K and $\varphi = 0.4 \text{ V}$ have shown that the degree of filling of the surface with the adsorbate, $\theta'_\text{R} = 0.3$, for solutions with concentrations of 10^{-4} , 5×10^{-5} , 2.5×10^{-5} , and $10^{-5} \text{ mole/litre}$ is attained within 10, 25, 47, and 170 s, respectively, and $\theta'_\text{R} = 0.35$ is attained within 16, 37, 74, and 107 s. Determine the exponent at the concentration given in the Roginsky-Zeldovich equation.

20. Studies into the adsorption of a 0.1*M* methanol solution on platinum at 293.2 K have yielded the following results:

$t_{\text{ads}}, \text{ s}$	0.5	1	2	5	10	20	50	100	200
θ'_R	0.09	0.20	0.32	0.44	0.56	0.69	0.77	0.80	0.82

Check whether the equation $\theta'_\text{R} = \beta + \frac{1}{\alpha f'} \ln t$ is applicable to the kinetics of methanol adsorption on platinum (plot θ'_R versus $\log t$) and calculate the adsorption rate constant if the process obeys the Roginsky-Zeldovich equation.

21. Studies into the adsorption of methanol on a platinum electrode at 284, 296, 308, 319, and 345 K have shown that the increase in the degree of filling of the electrode surface from $\theta'_\text{R} = 0.35$ to $\theta'_\text{R} = 0.4$ takes 5.0, 3.0, 2.0, 1.3, and 0.6 s, respectively. Calculate the mean activation energy of methanol adsorption on platinum at $\theta'_\text{R} \cong 0.375$.

Multivariate Problems

1. Determine the constants *a* and *b* in the Tafel equation if measurements of the potential of a cathode made of a particular material, with reference to the calomel electrode ($\varphi = 0.281 \text{ V}$), in a solution of a given composition at current densities i' and i'' have yielded the values of φ' and φ'' , respectively.

Variant	Electrode material	Electrolyte	$i', \text{ mA/cm}^2$	$i'', \text{ mA/cm}^2$	$\varphi', \text{ V}$	$\varphi'', \text{ V}$
1	Zinc	2.0 <i>N</i> H_2SO_4	5.0	0.2	1.325	1.157
2	Cadmium	1.3 <i>N</i> H_2SO_4	0.4	8.0	1.372	1.528
3	Lead	1.0 <i>N</i> H_2SO_4	0.2	0.8	1.360	1.432
4	Cobalt	1.0 <i>N</i> HCl	0.1	1.5	0.356	0.533
5	Nickel	1.0 <i>N</i> HCl	0.05	2.5	0.476	0.646
6	Tantalum	1.0 <i>N</i> H_2SO_4	0.02	5.0	0.753	1.065
7	Rhodium	2.0 <i>N</i> H_2SO_4	5.0	34.0	0.380	0.478
8	Tin	2.0 <i>N</i> H_2SO_4	0.1	5.0	1.097	1.294

2. Determine the constants a and b in the Tafel equation for the overvoltage of hydrogen evolution on a zinc electrode with surface area $S = 4 \text{ cm}^2$ from $2 \text{ N H}_2\text{SO}_4$. The zinc electrode potential ϕ with respect to 1 N calomel electrode being equal to -1.267 V , 9.5 mg Cu were deposited on the cathode of a copper coulometer within 60 min and at -1.279 V 5.94 mg Cu were deposited within 30 min .

Variant	Electrode material	Solution	$S, \text{ cm}^2$	$t, \text{ min}$	$m, \text{ mg}$	$\phi, \text{ V}$
2	Cadmium	$1.3 \text{ N H}_2\text{SO}_4$	5	50	9.90	1.453
				20	11.88	1.511
3	Tin	$2.0 \text{ N H}_2\text{SO}_4$	2	100	4.76	1.223
				10	9.90	1.375
4	Lead	$1.0 \text{ N H}_2\text{SO}_4$	3	10	5.94	1.554
				6	5.35	1.576
5	Nickel	1.0 N HCl	5	50	9.50	0.635
				60	57.01	0.705
6	Tantalum	$1.0 \text{ N H}_2\text{SO}_4$	1.6	60	4.76	1.026
				10	7.92	1.156

Complex Problems

1. The transformation of C_2H_4 in the reaction $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$ is 50% complete within 10 hours at 1073.2 K . Calculate the activation energy of the forward reaction (the end products are removed).

2. The activation energy of the reaction $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$ is $E_a = 252 \times 10^3 \text{ J}$. Calculate the temperature at which the yield of C_2H_2 within an hour equals half the amount theoretically possible when equilibrium is reached. Also calculate the time interval within which the above concentration will be attained at 1573 K .

3. Calculate the equilibrium yield in the reaction $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ at $1.01 \times 10^5 \text{ Pa}$ and 673.2 K , as well as the time it will take for the C_2H_6 yield to constitute 90% of the equilibrium value. The activation energy is $E_a = 182.7 \times 10^3 \text{ J}$, and the concentrations of C_2H_4 and H_2 are 1 mole/litre each.

4. Hydrogen and iodine react as follows: $\text{H}_2 + \text{I}_2 = 2\text{HI}$. The composition of the gas supplied for the synthesis is (%): H_2 32, I_2 48, inert gas 20. Determine the temperature at which the equilibrium mixture will contain 30% H_2 at $1.01 \times 10^5 \text{ Pa}$ if $\Delta G^\circ = 246.0 - 2.3 \log T + 10.7T$. Calculate the time after the shift if the degree of H_2 transformation at the calculated temperature is 30 and 18%, the reaction is of the second order, the rate constant k of the forward reaction at $T_1 = 556.2 \text{ K}$ is 0.000119, and at $T_2 = 781.2 \text{ K}$, $k = 3.58$. Plot the temperature dependence of the equilibrium yield and rate of the reaction.

Appendix

TABLE 1. Parachors of Atoms, Bonds, and Cycles

Atoms	$P \times 10^7,$ $J^{1/4} m^{5/2} \text{ mole}^{-1}$	Bond and cycle increments	$P \times 10^7,$ $J^{1/4} m^{5/2} \text{ mole}^{-1}$
Carbon	16.36	Bond	
Hydrogen		simple	0
at carbon	27.39	double homeopo- lar	33.78
at oxygen	17.79	triple	67.56
at nitrogen	22.23	semipolar	0
Oxygen	35.56	Cycle	
peroxide	37.87	three-membered	22.23
Nitrogen	31.11	four-membered	10.67
Phosphorus	72.01	five-membered	5.33
Arsenic	96.01	six-membered	1.42
Antimony	120.90	seven-membered	-7.11
Sulphur	88.01		
Selenium	112.01		
Fluorine	45.34		
Chlorine	97.79		
Bromine	122.68		
Iodine	160.02		
Boron	38.23		
Silicon	55.12		
Tin	114.68		
Mercury	122.68		

NOTE: Attachment of two or more negative X groups (Cl, CN, COOR, OR, etc.) to one and the same atom C, N, or S reduces the parachor by an average of 5.33×10^{-7} units for $-\text{CHX}_2$, 10.67×10^{-7} units for $-\text{CX}_3$, and 16.00×10^{-7} units for CX_4 .

TABLE 2. Functions ($H_T^\circ - H_{298}$) for Some Substances (kJ/mole)

T, K	H ₂ O	H ₂	O ₂	CO ₂	CO	COCl ₂	HCl
300	0.084	0.054	0.054	0.084	0.084	0.126	0.084
400	3.743	2.958	3.025	4.017	3.012	6.234	2.971
500	6.945	5.883	6.084	8.326	5.941	12.845	8.899
600	10.544	8.812	9.242	12.929	8.953	19.790	8.870
700	14.226	11.749	12.502	17.782	12.050	27.029	11.841
800	18.033	14.703	15.841	22.803	15.188	34.434	14.853
900	21.966	17.673	19.246	28.033	18.410	42.007	17.949
1000	26.024	20.677	22.707	33.388	21.714	49.706	21.046

T, K	NH ₃	NH ₄ Cl	Na ₂ CO ₃	NaOH	S ₈	H ₂ S
300	0.084	0.159	0.205	0.109	0.042	0.084
400	3.807	9.680	11.996	6.350	4.640	3.556
500	7.824	23.470	26.295	13.300	8.565	7.196
600	12.217	33.090	40.593	34.200	2.150	11.046
700	16.862	43.820	57.612	42.748	5.498	15.021
800	21.840	—	74.630	51.296	3.341	19.205
900	27.112	—	91.251	59.727	5.174	23.514
1000	32.635	—	107.872	68.157	7.019	28.033

TABLE 3. Diffusion Potential at 298 K

Electrolyte	$\varphi \times 10^3$, V	Electrolyte	$\varphi \times 10^3$, V
1M HCl KCl _{sat}	14.1	0.01M HCl 0.1M KCl	26.9
0.1M HCl KCl _{sat}	4.6	0.01M HCl 0.1M KCl	9.1
0.01M HCl KCl _{sat}	3.0	0.1M NaOH 0.1M KCl	-19.2
0.01M HCl + +0.09M NaOH KCl _{sat}	2.1	0.01M NaOH 0.1M KCl	-4.5
0.1M KCl KCl _{sat}	1.8		

TABLE 4. Molecular Constants of Diatomic Molecules

ω_e = intrinsic wave number; x_e = anharmonicity constant;
 B_e = rotational constants; r_e = equilibrium internuclear distance;
 D_{298} = dissociation energy

Molecule	ω_e , cm^{-1}	$x_e \times 10^3$	B_e , cm^{-1}	r_e , Å	D_{298} , kJ/mole
Br_2	325.3	3.31	0.0821	2.28	192.9
BrCl	444.27	4.15	0.152	2.13	215.0
Cl_2	559.75	4.81	0.244	1.987	242.3
ClF	786.15	7.84	0.516	1.63	252.5
CO	2169.81	6.11	1.931	1.128	1075.0
DF	2998.19	15.3	11.00	0.818	273.2
DI	1639.6	12.1	32.84	1.61	298.5
F_2	917.55	12.9	0.89	1.41	159.0
FO	1060	14.6	1.104	1.32	215.7
H_2	4400.4	27.4	60.86	0.741	435.9
HBr	2648.97	17.1	8.465	1.414	366.5
HCl	2990.9	17.65	10.59	1.274	431.4
HF	4138.7	21.7	20.95	0.917	566.1
HI	2309.01	17.2	65.11	1.61	298.4
I_2	214.55	2.87	0.037	2.66	151.0
IO	681.47	6.3	0.340	1.868	222.0
K_2	92.96	3.82	0.056	3.92	53.14
N_2	2358.03	6.00	1.998	1.098	945.6
NO	1904.4	7.45	1.704	1.151	631.0
O_2	1580.19	0.76	1.445	1.207	498.7
OH	3737.9	29.7	18.895	0.969	428.0
P_2	780.69	3.61	0.303	1.893	489.1

Answers

Chapter 1

1. $O_2 (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py})^2 (\pi_{2pz})^2 (\pi_{2py}^*)^1 (\pi_{2pz}^*)^1$; $u = 2$; $O_2^+ (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py})^2 (\pi_{2pz})^2 (\pi_{2py}^*)^1$; $u = 2.5$; $O_2^- (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py})^2 (\pi_{2pz})^2 (\pi_{2py}^*)^1 (\pi_{2pz}^*)^1$; $u = 1.5$. 2. 1st; the molecule lacks magnetic properties. 3. 79. 4. 2nd. 5. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2$; $u = 0$; $r_e = \infty$. $\epsilon = 0$. 6. 2nd. 7. CO^+ , BO , and CN ; $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2py})^2 (\pi_{2pz})^2 (\sigma_{2px})^1$; $u = 2.5$; ${}^2\Sigma$. 8. BN , BO , CO .

2.

j	$\epsilon \times 10^{22}, J$	$\tilde{\nu}, m^{-1}$	j	$\epsilon \times 10^{22}, J$	$\tilde{\nu}, m^{-1}$
0	0	1312.6	5	39.108	7 875.4
1	2.607	2625.1	6	54.751	9 188.0
2	7.822	3937.7	8	93.858	11 813.1
3	15.643	5250.3	9	117.323	13 125.7
4	26.072	6562.8	10	143.395	14 438.3

4.

j	$\epsilon_{rot} \times 10^{22}, J$	j	$\epsilon_{rot} \times 10^{22}, J$
0	0	5	125.805
1	8.387	6	176.127
2	25.161	7	234.836
3	50.322	8	301.932
4	83.870	9	377.415

T, K	300	500	1000
$\epsilon_{trans} \times 10^{22}, J$	62.12	108.54	207.10

5.

j	$\tilde{\nu}, \text{ m}^{-1}$	j	$\tilde{\nu}, \text{ m}^{-1}$
0	4 222.4	5	25 334.6
1	8 444.9	6	29 557.0
2	12 667.3	7	33 779.5
3	16 889.7	8	38 001.9
4	21 112.2	9	42 224.0

6.

j	N_j/N_0	j	N_j/N_0	j	N_j/N_0
0	1	4	1.1877	7	0.0517
1	2.4384	5	0.5275	8	0.0116
2	2.7240	6	0.1849	9	0.0021
3	2.0768				

7.

j	$N_j \times 10^{-23}$	j	$N_j \times 10^{-23}$	j	$N_j \times 10^{-23}$
0	0.5902	4	0.7010	7	0.0305
1	1.4391	5	0.3113	8	0.0068
2	1.6077	6	0.1091	9	0.0012
3	1.2257				

Chapter 2

1. Linear; $D_{\infty h}$; σ ; C_{∞} ; s_{∞} ; i . 2. Plane triangle; D_{3h} ; σ ; C_3 , C_2 , S_3 . 3. Trigonal pyramid; C_{3v} , σ_v , C_3 . 4. Trigonal bipyramid; C_{3v} , C_3 , σ_v . 5. Square bipyramid; C_{4v} , C_4 , C_2 , σ_v , σ_d . 6. 2nd. 7. 6th. 8. $\hat{S}(C_n)x = x \cos \frac{2\pi}{n} + y \sin \frac{2\pi}{n}$; $\hat{S}(C_n)y = -x \sin \frac{2\pi}{n} + y \cos \frac{2\pi}{n}$; $\hat{S}(C_n)z = z$. 9. $\hat{S}(S_n)x = -x \sin \frac{2\pi}{n} + y \cos \frac{2\pi}{n}$; $\hat{S}(S_n)y = -y \cos \frac{2\pi}{n} + x \sin \frac{2\pi}{n}$; $\hat{S}(S_n)z = -z$.

Chapter 3

1. $4.265 \times 10^{-47} \text{ kg m}^2$. 9. $14.652 \times 10^{-47} \text{ kg m}^2$; $1.1344 \times 10^{-10} \text{ m}$. 10. $352.96 \times 10^{-22} \text{ J}$. 11. $0.2787 \times 10^{-10} \text{ m}$. 12. $43.580 \times 10^3 \text{ m}^{-1}$.

Chapter 4

1. $1.540 \times 10^{-10} \text{ m}$. 2. $18.80 \times 10^{-47} \text{ kg m}^2$; 297.7 m^{-1} . 3. $107.155 \times 10^{-138} (\text{kg m}^2)^3$. 4. $3.093 \times 10^{-134} (\text{kg m}^2)^3$. 5. $0.9433 \times 10^{-10} \text{ m}$; $106^\circ 29'$. 7. $I_A = I_B = 6.237 \times 10^{-47} \text{ kg m}^2$; $I_C = 7.111 \times 10^{-47}$; oblate symmetric top.

8.

j	k	$\epsilon \times 10^{22}, \text{ J}$	j	k	$\epsilon \times 10^{22}, \text{ J}$
0	0	C	2	2	4.902
1	0	1.782	3	0	10.692
1	1	1.671	3	1	10.581
2	0	5.346	3	2	10.248
2	1	5.235	3	3	9.694

9. 39.16. 10. $I_A = I_B = 147.317 \times 10^{-47} \text{ kg m}^2$; $I_C = 294.634 \times 10^{-47} \text{ kg m}^2$; $6.394 \times 10^{-135} (\text{kg m}^2)^3$.

Chapter 5

1. $9.597 \times 10^{-14} \text{ N/m}$. 2. $3.0004 \times 10^5 \text{ m}^{-1}$. 3. 0.0060. 4. $\epsilon_0 = 2.148 \times 10^{-22} \text{ J}$; $\epsilon_1 = 6.406 \times 10^{-22} \text{ J}$. 5. 22; $4.0677 \times 10^{-22} \text{ J}$; $\epsilon_{\max} = 94.154 \times 10^{-22} \text{ J}$; $E_b = 542.54 \times 10^3 \text{ J/mole}$. 6. 5.9×10^{-5} ; 5.334×10^{-2} . 7. 0.359; 0.736.

8.

v	$\epsilon \times 10^{20}, \text{ J}$	$(r - r_e) \times 10^{10}, \text{ m}$	
0	3.744	0.6380	0.8706
5	35.995	0.4714	1.3411
10	58.796	0.4160	1.8288
20	76.098	0.3839	4.5689

9. 3915.93, 3837.71, and 3831.49 cm^{-1} . 10. 4000.37, 4042.59, and 4084.81 cm^{-1} .

11.

j	N_j/N_A	j	N_j/N_A	j	N_j/N_A
0	0.051	5	0.119	9	0.009
1	0.137	6	0.076	10	0.004
2	0.186	7	0.042	11	0.002
3	0.191	8	0.021	12	0.0003
4	0.163				

12.

j	$\tilde{\nu}, \text{cm}^{-1}$	j	$\tilde{\nu}, \text{cm}^{-1}$	j	$\tilde{\nu}, \text{cm}^{-1}$
0	2906.01	5	2998.76	9	3060.00
1	2926.00	6	3015.15	10	3075.51
2	2945.27	7	3030.82	11	3086.30
3	2963.82	8	3045.77	12	3098.37
4	2981.65				

13. $5.1595 \times 10^{-47} \text{ kg m}^2$; $1.079 \times 10^{-10} \text{ m}$. 14. 4; 3; 6; 9. 15. $\nu_{as} = 870$; $\nu_s = 447$; $\delta = 240 \text{ cm}^{-1}$. 16. $\tilde{\nu}_{as} = 403 (3)$; $\delta_{as} = 129 (3)$; $\delta_s = 104 \text{ cm}^{-1} (2)$.

Chapter 6

1. $15.52 \times 10^3 \text{ J}$. 2. 2085.4 kJ/kg . 3. $3.24 \times 10^5 \text{ Pa}$; 1670.2 J . 4. 18.7498 kJ . 5. 359.637 K ; -400.37 J ; 400.34 J ; 1.335 kJ . 6. H_2 . 7. Ar ; 1383.19 K ; H_2 748.42 K ; H_2O 637.11 K . 8. 205.51 . 9. (a) 273 K ; $0.505 \times 10^5 \text{ Pa}$; 1573.3 kJ ; (b) 172 K ; $0.636 \times 10^5 \text{ Pa}$; 1259.9 kJ ; (c) 273 K ; $0.505 \times 10^5 \text{ Pa}$; 0 . 10. $22.914 \times 10^8 \text{ J}$. 11. $1.0212 \times 10^6 \text{ J}$. 12. $5.9547 \times 10^6 \text{ J}$. 13. $(H_{182.5}^\circ - H_0^\circ)_s = 14.375 \text{ kJ/mole}$; $(H_{182.5}^\circ - H_0^\circ)_{\text{liq}} = 28.426 \text{ kJ/mole}$. 14. $A = 0.0018095 \text{ J mole}^{-1} \text{ K}^{-4}$; $(H_{15.14}^\circ - H_0^\circ) = 23.8 \text{ J/mole}$; $(H_{182.5}^\circ - H_0^\circ)_s = 14.356 \text{ kJ/mole}$. 15. (a) -3.716 kJ ; (b) 0 ; (c) -5.596 kJ ; (d) -8.921 kJ . 16. $\Delta H_{298}^\circ = -214.78 \text{ kJ}$; $\Delta U_{298} = -209.82 \text{ kJ}$. 17. $\Delta H_{298}^\circ = 214.78 \text{ kJ}$; $\Delta U_{298} = -209.82 \text{ kJ}$. 18. $\Delta H_{f, 298}^\circ = -74.88 \text{ kJ}$; $\Delta U_{f, 298} = -72.40 \text{ kJ}$. 19. -854.28 kJ . 20. -644.97 kJ . 21. -125.07 kJ . 22. (a) 83.01 kJ ; (b) -451.68 kJ ; (c) -826.84 kJ ; (d) 34.70 kJ . 23. (a) 10.49 kJ ; (b) -493.14 kJ ; (c) -562.50 kJ ; (d) -631.21 kJ ; (e) -64.85 kJ . 24. (a) -5156.78 kJ/mole ; (b) -5149.14 kJ/mole . 25. -5061.06 kJ . 26. -231.18 kJ . 27. -6.98 kJ . 29. -12.40 kJ/mole ; 19.9% . 30. -55.938 kJ/mole . 31. -524.90 kJ/mole . 32. -2884.0 kJ/mole . 33. -89.76 kJ . 34. -288.06 kJ . 35. $\Delta H_T^\circ = -237.644 \times 10^3 - 13.01 T +$

$2.883 \times 10^{-3} T^2 - \frac{1.713 \times 10^5}{T}$; -246.421 kJ; from 298 to 2500 K. 36. $\Delta H_T^\circ = 131.99 \times 10^3 + 8.54 T - 3 \times 81 \times 10^{-3} T^2 - \frac{8.502 \times 10^5}{T}$; 135.87 kJ. 37. 1.962 kJ/mole. 38. 36.70 kJ/mole. 39. -694.91 kJ/mole. 40. -78.87 kJ. 41. -298.26 kJ. 42. -60.826 kJ. 43. $C_P^\circ = 2.08 + 269.27 \times 10^{-3} T - 96.61 \times 10^{-6} T^2$.

Chapter 7

1. -166.5 J. 2. -125 J. 3. 2000, 1490, and 1730 J. 4. (1) 2.42; (2) 4.07 J mole $^{-1}$ K $^{-1}$. 5. 62 J mole $^{-1}$ K $^{-1}$. 6. 5.5 J mole $^{-1}$ K $^{-1}$. 7. 6.3 J mole $^{-1}$ K $^{-1}$. 8. -15.16 J mole $^{-1}$ K $^{-1}$. 9. 233 J mole $^{-1}$ K $^{-1}$. 10. 8.2×10^{-5} J mole $^{-1}$ K $^{-1}$. 11. 15.341 J mole $^{-1}$ K $^{-1}$. 12. 11.51 J mole $^{-1}$ K $^{-1}$. 13. $\Delta H = 7009.038 \times 10^3$ J; $\Delta U = 6543.811 \times 10^3$ J; $\Delta S = 20.756 \times 10^3$ J/deg. 14. 142 J mole $^{-1}$ K $^{-1}$. 15. 3.52 J mole $^{-1}$ K $^{-1}$. 16. 302 J mole $^{-1}$ K $^{-1}$. 17. 1.2 J mole $^{-1}$ K $^{-1}$. 18. (1) $\Delta S = -32.56$ J mole $^{-1}$ K $^{-1}$; (2) $S = 61.55$ J mole $^{-1}$ K $^{-1}$; (3) $\Delta S = 317.10$ J mole $^{-1}$ K $^{-1}$. 19. $\Delta S = -35.62$ J mole $^{-1}$ K $^{-1}$. 20. (1) -55 J mole $^{-1}$ K $^{-1}$; (2) 176 J mole $^{-1}$ K $^{-1}$; (3) -166 J mole $^{-1}$ K $^{-1}$; (4) -13.2 J mole $^{-1}$ K $^{-1}$. 21. 103.8 J mole $^{-1}$ K $^{-1}$. 22. 3325 J mole $^{-1}$ K $^{-1}$. 23. 243.6 J mole $^{-1}$ K $^{-1}$. 24. 56.87 J mole $^{-1}$ K $^{-1}$. 26. Isothermal expansion, $\Delta S_1 = nR \ln \frac{2V - nb}{V - nb}$; isochoric cooling, $\Delta S = \Delta S_1 + \Delta S_2 = nR \ln \frac{2V - nb}{V - nb} + \frac{3}{2} n \left(1 - \frac{na}{3RV T_0} \right)$. 28. 1130 J/mole. 29. (1) -134 J/mole; (2) 0; (3) 2330 J/mole. 30. -619.72 J; 5875.38 J; 6495.1 J. 31. $\Delta G_1 = 0$; $\Delta G_2 = -328.02$ J/mole; $\Delta G_3 = 0$. 32. $\Delta G = -108$ J/mole; $\Delta H = -5840$ J/mole; $\Delta S = -21.3$ J/(mole K). 33. 96.7 J/mole. 34. $A = -4476$ J; $\Delta U = 0$; $\Delta H = 0$; $\Delta S = -5.78$ J mole $^{-1}$ K $^{-1}$; $\Delta G = -4476$ J/mole; $\Delta A = -4476$ J/mole. 36. (a) -2879 J; (b) graphite; (c) yes, at a pressure of at least 2500 atm. 38. $\Delta G = -21755 + 0.74 \ln T - 7.5 T - 7 \times 10^{-5} T^2$. 42. $\Delta U = -469$ J/mole; $\Delta H = -652.5$ J/mole; $\Delta A = -3820$ J/mole; $\Delta G = -3621$ J/mole; 188.8 K; $V = 3.71$ m 3 .

Chapter 8

1. 2.4993×10^7 . 2. 1.1733×10^2 . 3. 1.0117. 4. 2. 5. 5.9335×10^9 . 6. 1.2025×10^{10} . 7. 5.5215×10^{11} . 8. 6.5424×10^9 . 9. 1.4086×10^8 . 10. 220.4288. 11. 2.1926. 12. 1. 13. 680.7935×10^8 . 14. 2.5857×10^{11} . 15. 12.4715 kJ/mole. 16. 8.3143 kJ/mole. 17. 2.173 kJ/mole. 18. $(U_{1000} - U_0) = 22.959$ kJ/mole; $(H_{1000}^\circ - H_0^\circ) = 31.273$ kJ/mole. 19. $(U_{1000} - U_0) = 22.959$ kJ/mole; $(H_{298}^\circ - H_0^\circ) = 31.273$ kJ/mole; $(H_{1000}^\circ - H_{298}^\circ) = 22.591$ kJ/mole. 20. $C_{P, 298}^\circ = 29.3368$ J mole $^{-1}$ K $^{-1}$; $C_{P, 1000}^\circ = 34.6000$ J mole $^{-1}$ K $^{-1}$. 21. 7.5534 kJ/mole; 10.0311 kJ/mole. 22. 8.1233 kJ/mole; 10.6010 kJ/mole. 23. 12.4715 J mole $^{-1}$ K $^{-1}$. 24. 12.4715 J mole $^{-1}$ K $^{-1}$. 25. 38.819 J mole $^{-1}$ K $^{-1}$. 26. 72.076 J mole $^{-1}$ K $^{-1}$. 27. 35.639 J mole $^{-1}$ K $^{-1}$. 28. $C_P^\circ = 60.356 + 97.754 \times 10^{-3} T - 54.09 \times 10^{-6} T^2$. 29. 40.524 J mole $^{-1}$ K $^{-1}$. 30. 53.909 J mole $^{-1}$ K $^{-1}$. 31. 1260. 32. 999.6. 33. 1.0135×10^5 Pa. 35. The CO $_2$ molecule is linear, and the SO $_2$ molecule is nonlinear. 36. $C_V = 12.4715$ J mole $^{-1}$ K $^{-1}$; $(U_{298} - U_0) = 3.7166$ kJ/mole; $S_{298}^\circ = 163.962$ J mole $^{-1}$ K $^{-1}$. 37. 48.1261 J mole $^{-1}$ K $^{-1}$.

38.	T	298	1000	3000
	S_{vibr}	0.0014	1.572	8.353

39. $210.884 \text{ J mole}^{-1} \text{ K}^{-1}$. 40. $-192.1023 \text{ J mole}^{-1} \text{ K}^{-1}$. 41. $-157.1403 \text{ J mole}^{-1} \text{ K}^{-1}$; -4.683 kJ/mole . 43. $188.721 \text{ J mole}^{-1} \text{ K}^{-1}$. 44. 219.4. 45. 0.0108.

46.

j	N_j/N_A	j	N_j/N_A	j	N_j/N_A
0	0.05119	6	0.07752	11	0.00137
1	0.13862	7	0.04369	12	0.00044
2	0.18826	8	0.02183	13	0.00012
3	0.19386	9	0.00971	14	0.00003
4	0.16550	10	0.00385	15	0.00000
5	0.12124				

Chapter 9

1. 0.288 litre. 2. 78; C_6H_6 . 3. 0.465 kg; 8.3 kg/m^3 ; 0.0179 kg/m^3 . 4. 376.7 kg. 5. 757 mm Hg. 6. Cl_2 74.1%; Br_2 13.7%. 7. 0.987 atm; $V_{\text{O}_2} = 16.56 \text{ m}^3$; $V_{\text{N}_2} = 58.44 \text{ m}^3$. 8. 4.53 kg. 9. 396 K. 15. $7.6 \times 10^2 \text{ m/s}$. 16. $\sigma_{\text{N}_2} = 3.64 \times 10^{-10} \text{ m}$; 750 K. 17. $Z = 8.05 \times 10^{11}$; $Z' = 9.1 \times 10^{32}$; $Z'' = 1.18 \times 10^{25}$; 0.261 atm. 18. 55%. 19. 0.37 litre. 20. 4.1%. 21. 0.5986, 0.2676, and 0.1338 atm. 22. 5.4%; 19.8%; 1.054; 1.198. 23. 55.55

Chapter 10

1. $18.22 \times 10^{-6} \text{ m}^3/\text{mole}$. 2. $96.3576 \times 10^{-6} \text{ m}^3/\text{mole}$. 3. 1.17 D. 4. 2.77 D; $0.92 \times 10^{-29} \text{ K m}$. 5. $27.453 \times 10^{-6} \text{ m}^3/\text{mole}$; $27.193 \times 10^{-6} \text{ m}^3/\text{mole}$. 6. $21.334 \times 10^{-6} \text{ m}^3/\text{mole}$; $21.140 \times 10^{-6} \text{ m}^3/\text{mole}$. 7. $\text{CH}_3\text{COOCH}_2-\text{CH}=\text{CH}_2$. 8. 0. 9. 2.018 m^3 . 10. $0.8995 \times 10^{-3} \text{ kg/cm}^3$. 11. $0.0390 \text{ kg}^{1/4} \text{ m}^3 \text{ s}^{-1/2} \text{ kmole}^{-1}$. 12. 1. 13. $\text{CH}=\text{CH}$

$\begin{array}{c} | \\ \text{CH}=\text{CH} \\ | \end{array} \text{NH pyrrone. 14. } \sigma_T = 0.6988 - 0.12377 \times 10^{-3} T; -0.12377 \times 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}.$

15. $-12.377 \times 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}$. 16. $69.76 \times 10^{-3} \text{ J/m}^2$.

17. $\frac{1}{\eta} = \frac{16.5 \times 10^6}{d} - 13.226 \times 10^3$; $\eta = 0.1877 \times 10^{-3}$. 18. $E_\eta = 10.4895 \text{ kJ/mole}$; $\eta = 8.8145 \times 10^{-6} e^{\frac{10489.5}{RT}}$. 19. 28.074 kJ/mole. 20. $H_{\text{evap}} = 51.87 \times 10^3 - 50.4T + 0.5 \times 10^{-3} T^2 + \frac{9.87 \times 10^5}{T}$. 21. $\Delta H_{340} = 49.335 \text{ kJ/mole}$; $\Delta S_{340} = 145 \text{ J mole}^{-1} \text{ K}^{-1}$. 22. 62.24 kJ/mole. 23. 85.44 kJ/mole. 24. 508.690 kJ/mole. 25. 440.718 kJ/mole.

Chapter 11

3. $1.947 \times 10^7 \text{ Pa}$. 4. 273 K; $\Delta H_1 = 2.504 \times 10^3 \text{ kJ/kg}$; $\Delta H_2 = 2.491 \times 10^3 \text{ kJ/kg}$; 573 K; $\Delta H_1 = 1.712 \times 10^3 \text{ kJ/kg}$; $\Delta H_2 = 1.403 \text{ kJ/kg}$. 5. $\Delta H = 37.3 \text{ kJ/mole}$; boiling point = 305.16 K. 6. $A = 11.635$, $B = 1.68 \times 10^4$. 7.

$Q = 245 \text{ kJ}$. 8. $\Delta H = 19.04 \text{ kJ/mole}$. 9. $P = 4.123 \times 10^4 \text{ Pa}$, $\Delta H = 49.95 \text{ kJ/mole}$. 10. 283.17 K , $2.13 \times 10^3 \text{ Pa}$, $\Delta H_{\text{subl}} = 44.27 \text{ kJ/mole}$; $\Delta H_{\text{evap}} = 31.95 \text{ kJ/mole}$; $\Delta H_{\text{fus}} = 12.32 \text{ kJ/mole}$. 12. 95—true molecular weight of CH_3COOH ; 60. The obtained value indicates that CH_3COOH in the vapour phase is partially associated. 13. 5.998 Pa . 14. $P_1^0 = 5.81 \times 10^3 \text{ Pa}$, $P_2^0 = 5.03 \times 10^3 \text{ Pa}$. 16. $T_1 = 335.6 \text{ K}$, $T_2 = 408.4 \text{ K}$, $T_3 = 452.4 \text{ K}$; $\Delta H_{\text{fus}(1)} = 56.52$, $\Delta H_{\text{fus}(2)} = 62.4$, and $\Delta H_{\text{fus}(3)} = 46.48 \text{ kJ/kg}$. 17. (a) 157°C ; (b) 302°C . 21. 519.23 kJ/kg . 23. $\Delta S \simeq 26$. 24. (1) $\log P = -\frac{4110}{T} + 2.18$; (2) $\Delta H = 43\,340 \text{ J}$. 25. 1.823 litre . 26. $\Delta H = 10\,100 - 8.1T$, $\Delta H = 93.72 \text{ J mole}^{-1} \text{ K}^{-1}$. 27. 468 mm Hg . 28. $28\,367 \text{ J/mole}$; 34.7°C . 29. $361\,064.0 \text{ J/mole}$. 30. $2545 \text{ K} \log P = \frac{1.648 \times 10^4}{T} + 9.348$. 31. 28.8°C .

Chapter 12

1. 3.128 mole/litre ; 3.414 mole/kg ; 0.058 ; 26% . 2. 8.732 mole/litre ; 15.31 mole/kg ; 0.216 . 3. $0.0105 \text{ mole/mole H}_2\text{O}$; $0.5534 \text{ mole/litre}$; $0.9016 \text{ cm}^3/\text{g}$. 4. 789.3 g ; $0.98 \text{ cm}^3/\text{g}$. 5. 1.134 g/cm^3 . 6. 0.44 cm^3 . 7. 4.16 cm^3 ; $1.17 \text{ cm}^3/\text{g}$; $1.260 \text{ cm}^3/\text{g}$. 8. $27.3 \text{ cm}^3/\text{mole}$. 9. $8.75 \text{ cm}^3/\text{mole}$. 10. 19.93 ; $23.14 \text{ cm}^3/\text{mole}$. 11. $39.72 \text{ cm}^3/\text{mole}$. 12. $20.44 \text{ cm}^3/\text{mole}$. 13. 234 g . 14. $7.918 \text{ cm}^3/\text{mole}$. 15. $18 \text{ cm}^3/\text{mole}$. 17. -0.421 ; -0.231 ; -0.148 ; -1.730 ; -0.986 ; -0.619 . 18. -0.0765 ; -0.052 ; -0.047 ; -0.3198 ; -0.217 ; -0.196 . 19. 4430.86 J ; $\Delta \bar{H}_1 = 1188.26 \text{ J/mole}$; $\Delta \bar{H}_2 = 6263.45 \text{ J/mole}$. 20. 6351.31 J/mole ; $\Delta H = 230.96 \text{ J}$. 21. $\Delta \bar{H}_1 = -28\,200.16 \text{ J/mole}$; $\Delta \bar{H}_2 = -1832.59 \text{ J/mole}$; $\Delta H = -95\,596.03 \text{ J}$. 22. $\Delta H = 41\,798.16 \text{ J/mole}$. 24. 3740 J/mole . 25. -718 kJ . 26. $\Delta S_m = R(x_{\text{Ag}} + x_{\text{Au}} \ln x_{\text{Au}}) - 5.03x_{\text{Ag}}x_{\text{Au}}$; $4.34 \text{ J mole}^{-1} \text{ K}^{-1}$. 27. $\mu_{\text{Fe}} = \mu_{\text{Fe}}^0 + RT \ln x_{\text{Fe}} - 2095x_{\text{Ni}}^0$; $\mu_{\text{Ni}} = \mu_{\text{Ni}}^0 + RT \ln x_{\text{Ni}} - 2095x_{\text{Ni}}^2$. 28. 0.903 . 29. 0.583 ; 0.246 . 30. 1.93 . 31. $a = 0.920$; $\gamma = 0.989$. 32. 0.2499 . 33. 1.52 . 34. 161 . 35. 35.41 . 36. 16.89 J/mole . 38. 1903.72 J ; 40. -8600 J/mole . 41. -1330 J/mole . 42. 660 J/mole . 43. $9.68 \text{ J mole}^{-1} \text{ K}^{-1}$. 44. $\Delta \mu = -157\,500 \text{ J/mole}$. 45. $\Delta T = 42^\circ\text{C}$.

Chapter 13

1. 0.00036 . 2. $7338 \times 10^3 \text{ Pa}$. 3. $5.75 \times 10^4 \text{ Pa}$. 4. 119.6 ; 2.04% . 5. 1.85 . 6. 1.49% . 7. 57.5% . 8. 194.5 . 9. $1.0096 \times 10^5 \text{ Pa}$. 10. 2.63 . 11. 8 atoms . 12. 138.8 . 13. 373.18 . 14. 0.08 . 15. 152.8 . 16. 0.0248 kg . 17. 32.7 ; 238.7 . 18. 2.96 ; 2.53 . 19. 7.39 ; $111.3 \times 10^3 \text{ J/kg}$. 20. 1.154 mole/litre . 21. $27.07 \times 10^5 \text{ Pa}$. 22. 379.52 K ; $1.93 \times 10^6 \text{ Pa}$. 23. 271.47 K . 24. 561.3 Pa . 25. 272.17 K . 26. $0.865 \text{ mole/kg H}_2\text{O}$. 27. 92.19 . 28. $\text{C } 93.7\%$; $\text{H } 63\%$; 128 . 29. 373.62 ; 3124 Pa . 30. $2.56 \times 10^6 \text{ Pa}$. 31. 87.64 . 32. $x_{\text{N}_2} = 1.16 \times 10^{-4}$; $x_{\text{O}_2} = 0.59 \times 10^{-4}$. 33. 15.8 . 34. 0.01032 kg . 35. O_2 33.75% ; N_2 16.16% ; Ar 1.95% ; CO_2 2.14% . 36. $0.458 \times 10^{-3} \text{ m}^3$. 37. 16192.08 J/mole . 40. 0.88 g/litre . 41. 117 ; 0.03558 . 42. $K = c_1^{0.515}/c_2 = 2.192$; 0.515 . 43. 17.73 g . 44. 5.85 litres ; 0.579 litre ; 0.0527 litre . 45. $4.61 \times 10^{-3} \text{ g}$.

Chapter 14

1. 0.823×10^4 ; 0.867×10^4 ; 0.224×10^4 ; $1.092 \times 10^4 \text{ Pa}$. 2. 3.38×10^4 ; $4.24 \times 10^4 \text{ Pa}$. 3. 0.43 and $0.85\% \text{ CS}_2$; 5.5×10^4 and $6.5 \times 10^4 \text{ Pa}$.

4.	T	293	313	353
	$(\Delta P/P) \times 100\%$	-9.65	-7.19	-5.59

5. 67.6%. 6. 0.248. 7. $x_{\text{CCl}_4}^v = 0.523$; $x_{\text{CCl}_4}^{\text{liq}} = 0.144$.

8. T 330 350 380 420

$x_{\text{C}_6\text{H}_6}^v$ 0.765 0.710 0.696 0.682

10. Vapours, 0.295 kg; liquid, 0.705 kg. 11. H_2O 0.223 kg. 12. 39.6 kJ/mole. 13. -3.4 kJ/mole. 15. $\gamma_{\text{CCl}_4} = 1.555$; $a_{\text{CCl}_4} = 0.9799$; $\gamma_{\text{C}_2\text{H}_5\text{OH}} = 1.876$; $a_{\text{C}_2\text{H}_5\text{OH}} = 0.6940$. 16. $\gamma_{\text{H}_2\text{O}} = 0.7699$; $a_{\text{H}_2\text{O}} = 0.3595$; $\gamma_{\text{HCOOH}} = 0.8785$; $a_{\text{HCOOH}} = 0.4682$. The departure from Raoult's law is negative. 17. 1.651 kg. 18. 3.18 kg. 19. 0.563 kg. 20. 0.555 kg. 21. 1.37 kg.

Chapter 15

1. 1500 K; 51% Ni; $m_{\text{liq}} = 0.0277$ kg; $m_s = 0.0443$; 1435 K. 4. 0.324 kg. 7. 8.8%; 70.5; 0.066 kg; 0.034 kg; 336.5 K; 327.6 K.

Chapter 17

1. 0.845; 0.543; 0.465; 1.333. 2. CO 1.447%; H_2O 59.858%; CO_2 37.013%; H_2 1.68%. 3. 0.2264 mole. 4. 0.01113; 0.1264. 5. 5.496×10^4 Pa, 0.535. 6. 0.932; 0.0352. 7. 0.542; 3.516×10^4 Pa. 8. 1.014; 1.871×10^{-2} . 9. 0.363; 5.768 mole/m³; 0.632×10^4 Pa. 10. 0.721; 1.586; 0.910. 11. 28.99×10^4 Pa. 12. 2527.5; 17.02. 13. 72.35×10^{-3} . 14. 0.00164. 15. 0.219; 0.0504; 0.912. 16. 0.148; 7.0866×10^4 Pa. 17. 1.1255×10^5 Pa. 18. 0.083. 19. 1.809. 20. -24.436 kJ. 21. -21.888 kJ. 22. PCl_5 will not dissociate. 23. -376.96 kJ. 24. -148.48 J. 25. -27.02 J. 26. -442.095 kJ; $\Delta H_T^\circ = -432.092 - 12.505 \times 10^{-3}T$ (kJ). 27. 4454.08 m³/mole; 387.81 m³/mole; -114.19 kJ. 28. 50.232 kJ. 29. -116.226 kJ. 30. 1.0402. 31. -72.170 kJ. 32. 110.997 kJ; 813.9 K. 33. -17.345 kJ; -22.270 kJ; 0.859 J/K. 34. $\log K_P = -52.344 + \frac{0.6568 \times 10^5}{T^2} + \frac{47.2576 \times 10^3}{T} + 2.6244 \log T - 1.0241 \times 10^{-3}T$; 7.614×10^9 . 35. 1154.25 K. 36. $\log K_P = \frac{0.2732 \times 10^5}{T^2} - \frac{9.6356 \times 10^3}{T} - 1.2905 \log T + 12.5205 - 0.2183 \times 10^{-3}T$; 1.879. 37. 177.455 kJ; 2.463×10^{33} . 38. 73.633 kJ; $\log K_P = -\frac{3.846 \times 10^3}{T} - 0.3904$. 39. 0.01082; $x_{\text{C}_6\text{H}_6} = x_{\text{C}_6\text{H}_4(\text{CO}_2)_2} = 0.086$; $x_{\text{C}_6\text{H}_5\text{CH}_3} = 0.828$. 40. 5.2518; $x_{\text{C}_6\text{H}_6} = x_{\text{C}_6\text{H}_4(\text{CH}_3)_2} = 0.8217$; $x_{\text{C}_6\text{H}_5\text{CH}_3} = 0.1783$. 41. 29.97. 42. 247.5. 43. 3.36×10^4 Pa; 9.44×10^4 Pa. 44. 1.059×10^{-2} . 45. 3.293. 46. 492.2 K. 47. 8.357×10^5 . 48. 0.173. 49. 2.532×10^5 . 50. 4.116×10^4 . 51. 1.2787. 52. 31.109. 53. CH_2Cl_2 0.090; Cl_2 0.001; CHCl_3 0.320; HCl 0.499; CCl_4 0.090.

Chapter 18

1. $\beta = 3.727 \times 10^{-3}$ mho. 2. $\kappa = 8.135$ mho m⁻¹. 4. $t_- = 0.53$. 5. $\lambda_+ = 5.018$; $\lambda_- = 6.562$ mho m². 6. $\lambda_{\text{ClO}_4^-} = 5.907$ mho m². 10. 0.101 mole/litre. 11. 38.8 mho m². 12. $K_a = 1.79 \times 10^{-4}$; pH 4.32. 13. $K_a = 1.75 \times 10^{-5}$. 14. $c_{\text{H}^+} = 1.388 \times 10^{-3}$ mole/litre. 15. 1.12×10^{-5} g-equiv/litre. 16. $L_1 = 1.21 \times 10^{-3}$; $L_2 = 2.33 \times 10^{-4}$ mole/litre.

17. c , mole/litre	λ_{calc}	λ_{exp} , mho m^2
5×10^{-4}	12.44	12.45
0.1	9.82	10.67

18. $a_{\text{Na}_2\text{SO}_4} = 3.64 \times 10^{-4}$; $a_{\text{HCl}} = 6.36 \times 10^{-3}$. 19. $I = 0.14$; $\gamma_{\text{Na}^+} = 0.827$; $\gamma_{\text{La}^{3+}} = 0.25$. 20. 0.967. 22. $\Delta H = -1460$ J. 23. -132.8 kJ/mole. 24. -111 J/mole. 39. 55.94 kJ. 40. 1.08×10^{-3} , 5.66×10^{-4} . 41. 244.0. 42. 136.3. 43. -17.8 ; -12.5 kJ/mole. 44. 56.5 kJ/mole. 45. 0.01023. 46. -11.35 kJ/mole.

Chapter 19

3. 0.437 V. 4. 0.925 V. 5. 2.99. 6. 0.11 V. 8. -0.059 V. 9. 2.121 V. 10. $E_1 = 0.631$; $E_2 = 0.261$ V. 12. 6×10^{-2} . 13. $K_1 = 6.92 \times 10^{25}$; $K_2 = 3.44 \times 10^{15}$. 15. 0.722 V. 17. 0.321. 18. 0.458 V. 19. 0.133. 20. 0.049 V. 21. $a_{\text{Pb}} = 0.0057$; $\gamma_{\text{Pb}} = 0.297$. 22. $\varphi_{[\text{Ti}]/\text{Hg}, \text{Ti}^+} = -0.333$ V; $E = 0.003$ V. 23. $q = 21.05$ kJ/mole; $\Delta H = 195.5$ kJ/mole; $E = 1.083$ V. 25. $\Delta H = 6.5$ kJ/mole. 27. $a_{\text{Ti}} = 0.0628$; $\Delta G_{\text{Ti}}^m = -856$ J/mole. 28. $\Delta H_{\text{Ti}}^m = -1.459$ kJ/mole; $q = 0.121$ kJ/mole. 29. $a = 0.368$. 33. 1.00×10^{16} ; 1.44×10^{83} ; 5.8×10^{-7} . 34. 34.6 atm; 0.691; 44.3 atm; 0.443. 35. 119 kJ/mole; 1.229 V.

Chapter 20

1. $\Gamma = 7.1 \times 10^{-3}$ mm Hg; $K_1 = 36$ ml g^{-1} . 2. $\Gamma_1 = 18.6$. 3. $S = 449$ m^2 . 5. $\Gamma = 0.129$ g. 6. $\Gamma_\infty = 1.706$; $K = 9.56 \times 10^{-4}$. 7. $\Gamma_\infty = 4.33 \times 10^{-10}$; $K = 0.07$; $\Gamma = 3 \times 10^{-10}$ mole/ cm^2 . 8. $S = 12.22$ \AA^2 . 12. $s_{\text{sp}} = 0.21$ m^2/g . 13. $s_{\text{sp}} = 199.5$ m^2/g . 16. $\Delta H = 28.5 \times 10^3$ J/mole. 17. $\Delta H = 22.2 \times 10^3$ J/mole.

Chapter 21

1. 43.2 years. 2. 5.3×10^{-5} ; 4.35×10^4 min. 3. 0.0515 min^{-1} . 4. 2.65×10^{-4} ; 1530 min. 5. First; 2.7×10^{-3} min^{-1} . 6. 30 min. 7. 2.55×10^{-8} s. 8. 3.75 min. 9. 52%. 10. 7.36 min. 13. 0.7544; 23.8 h; 238.5 h. 14. 0.86 mole^{-1} min^{-1} litre. 15. 0.07 mole/litre. 16. 25%; 33.3%; 38%; 100%. 20. First. 21. First. 22. 1.5th. 23. First; 0.0123 min^{-1} . 25. First; 0.040 h^{-1} . 26. First; 4.19×10^{-4} min^{-1} . 27. 5.31×10^{-3} min^{-1} g-equiv $^{-1}$ litre. 28. Third. 29. Second; 11.6 min^{-1} g-equiv $^{-1}$ litre. 30. Second; 2.35 min^{-1} g-equiv $^{-1}$ litre. 31. Second; 0.0383 s^{-1} g-equiv $^{-1}$ litre. 32. First; 1.5×10^{-3} s^{-1} ; 460 s.

Chapter 22

1. $k_1 = 0.00422$; $k_2 = 0.00139$; $K_{\text{eq}} = 0.30$. 3. $k_1 = 1.84 \times 10^{-5}$ min^{-1} . 4. $k_1 = 0.01637$ min^{-1} ; $k_2 = 0.000334$ min^{-1} . 5. $k = 0.412$ mole^{-1} min^{-1} ml. 6. $k_1 = 0.035$ min^{-1} ; $k_2 = 5.72 \times 10^{-5}$ min^{-1} . 7. $k_1 = 35.6 \times 10^{-4}$ litre mole^{-1} min^{-1} ; $k_2 = 1.12 \times 10^{-4}$ min^{-1} . 9. $k_1/k_2 = 6.65$. 10. $\tau_{1/2} = 27.3$ min^{-1} . 15. 64.8 Pa. 16. $t_{\text{max}} = 33.015$ min. The maximum amount of RaA is 3.49×10^{-9} g. After 5 hours there will be 1.68×10^{16} atoms of radon and 9.3×10^{12} atoms of RaA. 17. (a) 0.07 g; (b) 1.835 times. 18. $N_2/N_{10} = 0.635$; $N_3/N_{10} = 0.3$. 19. 2.48×10^{-4} s^{-1} ; 1.79×10^{-4} s^{-1} .

Chapter 23

1. 334.6 kJ/mole; $k_0 = 10^{27}$. 2. 94 920 J/mole; 8.71×10^{12} ; 1.42 min. 3. 0.0002. 4. 46.442. 5. $k_1:k_2:k_3 = 1:47.7:100.5$. 6. 350 K. 7. 16.37×10^{-3} min^{-1} ; 282 min. 8. 65 min. 9. 1.88. 10. 303 K. 11. $k_{283} = 7.05 \times 10^{-3}$; $k_{312} = 29 \times 10^{-3}$;

$k_{298} = 14.9 \times 10^{-3}$; 1.3. 12. 86×10^2 J/mole; 1330 min. 13. 1210 s. 14. 2.71×10^{-6} . 15. 1950 min. 19. $k_{373} = 0.00576$ litre mole $^{-1}$ s $^{-1}$; $k_{723} = 0.156$ litre mole $^{-1}$ s $^{-1}$. 20. $E_a = 362\,423.05 + 16.628T$ J/mole; $E_a = 375\,725.45$ J/mole. 21. 210 kJ/mole; $k_{01} = 10^{12.35}$; $k_{02} = 10^{12.54}$. 22. $\log k_1 = 33.210 - \frac{23\,045.6}{T}$; $\log k_2 = 34.343 - \frac{21\,068.8}{T}$.

Chapter 24

1. $Z_0 = 29.4 \times 10^{22}$; $Z_0 = 9.58 \times 10^{28}$; $l = 61.4 \times 10^{-7}$ cm. 2. $Z_{\text{act}} = 184 \times 10^{16}$; $t_{1/2} = 0.00104$ min. 3. $E_a = 128\,030.4$ J/mole. 4. $Z_0 = 4.78 \times 10^9$. 5. $k = 7.8 \times 10^{-9}$ s $^{-1}$. 7. $p = 0.205$; $E_a = 165\,953.9$ J/mole. 8. $p = 5.3 \times 10^{-10}$; $E_a = 46\,818.96$ J/mole. 9. $p = 5.3 \times 10^{-8}$; $E_0 = 54\,475.68$ J/mole. 10. $p = 63 \times 10^{-8}$; $E_a = 57\,237.12$ J/mole. 13. $k = 9.3 \times 10^{-9}$ cm 3 molecule $^{-1}$ s $^{-1}$. 14. $k = 1.25 \times 10^{-12}$ cm 3 molecule $^{-1}$ s $^{-1}$. 15. $k = 4.12 \times 10^{-21}$ cm 3 molecule $^{-1}$ s $^{-1}$. 16. $k = 0.298$ cm 3 mole $^{-1}$ s $^{-1}$. 17. 152.9. 18. 7×10^{-3} h $^{-1}$. 19. $\Delta H^\ddagger = 72\,174$ J/mole; $E_a = 74\,709.5$ J/mole. 20. $\Delta H^\ddagger = 36\,149.76$ J/mole; $\Delta S^\ddagger = 68.032$ J mole $^{-1}$ K $^{-1}$. 21. $K_P = 7.76 \times 10^{-3}$; $E_a = 1\,112.9$ J/mole; $K_P = 1.63 \times 10^3$; $\Delta H^\ddagger = -10\,794.7$ J/mole. 22. $\Delta H^\ddagger = 10\,836$ J/mole; $\Delta S^\ddagger = 84.010$ J/mole; $\Delta H^\ddagger = -280\,196.3$ J/mole. 23. (a) $k = 74$ s $^{-1}$; $t_{1/2} = 9.4 \times 10^3$ s; (b) $k = 1.7 \times 10^{-2}$ s $^{-1}$; $t_{1/2} = 41$ s; (c) $k = 3.8 \times 10^{-6}$ s $^{-1}$; $t_{1/2} = 50$ h. 24. $\Delta H^\ddagger = 121\,336$ J/mole; $E_a = 233\,467.2$ J/mole. 25. $k = 1.28 \times 10^{-14}$ cm 3 mole $^{-1}$ s $^{-1}$. 26. $k = 4.0 \times 10^{-8}$ s $^{-1}$; $\Delta S^\ddagger = -3.347$ J mole $^{-1}$ K $^{-1}$. 27. 110 457.6 J/mole; 124 683.2 J/mole; 39.33 J mole $^{-1}$ K $^{-1}$. 28. $k = 45.3$ cm 3 mole $^{-1}$ s $^{-1}$. 29. $p = 0.5 \times 10^{-3}$.

Chapter 25

1. 55.35. 2. 10^3 . 3. 281.9 kJ/mole. 4. $E_a = 287.7$ kJ. 5. 105.6 kJ mole $^{-1}$; 1 E = 112.5 kcal/mole. 6. The luminous flux will be sufficient; in one link, -46.2 kJ, and in the other, $+186.06$ kJ; 2.5 J/mole per mole HCl. 7. $w = k_2 (k_0/2k_3) \text{Cl}^{3/2}$. 8. $w = k_2 (k_0/k_3) \text{C}_2\text{H}_4\text{Cl}_2$. 11. $\gamma = 0.55$. 17. 24.6 kJ/mole. 18. $\gamma = 7.5$; $k = 6.3 \times 10^{-3}$ s $^{-1}$. 21. 254.7 kJ/mole. 22. 1041 kJ/mole. 23. 1912 kJ/mole.

Chapter 26

1. $k_{\text{mean}} = 3.86$; $D = 6 \times 10^{-2}$ cm 2 /h. 2. 7.2×10^{-6} mole or 8.8×10^{-4} g. 3. $V = 9$ cm 3 ; $t = 10.98$ min. 4. $t = 39$ min 38 s. 5. $c_s = 0.1031$ g/50 g; $k = 6.45 \times 10^{-2}$ min $^{-1}$; $\delta = 4.95 \times 10^{-4}$ cm. 6. 0.23g. 7. $k_{\text{mean}} = 5.0 \times 10^{-3}$ min $^{-1}$; $\delta = 19 \times 10^{-6}$ m. 8. $D = 0.24$ cm 2 /s. 9. $r = 24$; $m = 6.2 \times 10^{-3}$ g. 10. $D = 0.10$ cm 2 /s. 12. $D = 0.545$ cm 2 /s.

Chapter 27

1. 0.636 cm 3 mole $^{-1}$ s $^{-1}$. 2. 1.012 cm 3 mole $^{-1}$ s $^{-1}$. 3. $k_1 = 2.32 \times 10^{-4}$ cm 3 mole $^{-1}$ s $^{-1}$; $k_2 = 1.18 \times 10^{-3}$ cm 3 mole $^{-1}$ s $^{-1}$; $k_3 = 8.65 \times 10^{-3}$ cm 3 mole $^{-1}$ s $^{-1}$. 4. 1:1.17:1.11. 5. 3130 s. 6. 3145; 6329; 12 882 s. 7. 1.60×10^{-5} ; 1.59×10^{-5} ; 1.66×10^{-5} mole litre $^{-1}$ s $^{-1}$. 8. 1.585. 14. $k_0 = 1.34 \times 10^{-4}$ min $^{-1}$; $k_A = 5 \times 10^{-5}$ mole $^{-1}$ min $^{-1}$. 19. $G_a = 7.90 \times 10^{-4}$; $\alpha = 0.62$. 20. 32 litre mole $^{-1}$ s $^{-1}$. 21. 2.72 times. 22. $E_a = 161 - 0.284\phi$. 23. $\Delta H_W^\ddagger = 163$ kJ; $\Delta H_{\text{Mo}}^\ddagger = 205$ kJ;

$\Delta H_{\text{Fe}}^\ddagger = 200.9 \text{ kJ}$; $\Delta H_{\text{Os}}^\ddagger = 129 \text{ kJ}$. 24. $k_D = 3.1 \text{ s}^{-1}$; $E_a = 35.2 \text{ kJ/mole}$.
 28. $k_{\text{eff}} = 0.0025 \text{ s}^{-1}$; $k_{\text{true}} = 0.0032 \text{ s}^{-1}$. 29. $E_1 = 41.8 \text{ kJ/mole}$; $E_2 =$
 20.9 kJ/mole . 30. $\bar{\nu}_0 \ln \frac{1}{1-y} = \nu_0 y + 0.012$. 31. $\beta = 1$; $\alpha = 0.048$.

Chapter 28

1. 1.779 g. 2. $t = 1560 \text{ s}$ (26 min). 3. $t = 32\,906 \text{ s}$ (9 h 8 min 25 s). 4. $6.34 \times 10^9 \text{ J}$. 5. 80%. 6. 83.25%. 7. $5.6 \text{ cm}^3 \text{ O}_2$; 31.77 mg Cu; 126.9 mg I_2 ; $11.2 \text{ cm}^3 \text{ H}_2$.
 8. 92.7%. 9. 92.9%. 10. 313 A h; 21.8 litres O_2 .

11. i , A/cm ²	0.01	0.015	0.018	0.019	0.0193
$\Delta\phi$, V	0.0092	0.0189	0.0340	0.0524	—
12. i , A/cm ²	5	10	15	18	19
$\Delta\phi$, V	0.269	0.264	0.255	0.244	0.235
13. ϕ_k , V	-0.535	-0.505	-0.490	-0.485	-0.480
i/i_{lim}	0.99	0.92	0.74	0.62	0.42

14. 70.2% Cu; 29.8 A. 15. 66.6% Ni; 33.4% Co. 16. $a = 0.840 \text{ V}$; $b = 0.190 \text{ V}$;
 $\alpha = 0.305$. 19. $n = 1.0$. 20. $\alpha f' = 6.4$; $A = 0.2$; $k = 2 \text{ litre mole}^{-1} \text{ s}^{-1}$. 21. $E_a =$
 42 kJ.